

CALCITE DISSOLUTION KINETICS AND LAKE NEUTRALIZATION

HARALD U. SVERDRUP

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CALCITE DISSOLUTION KINETICS AND LAKE NEUTRALIZATION

A
DOCTORAL DISSERTATION
BY

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Abstract Models for the dissolution of minerals in acidic aqueous solution are discussed, and in particular the dissolution kinetics of calcite. The dissolution kinetics of other minerals such as dolomite, tricalciumsilicate, olivine and K-Feldspar are included for comparison. The kinetic expressions have been incorporated into a model for lake liming, that will predict the dissolution of a calcite powder when distributed in a lake. A sensitivity analysis of lake neutralization is discussed. A model that describes the reacidification of a limed lake is discussed. The model is based on a mass balance for the lake, and considers the long term dissolution-deactivation of residual calcite on the lake bottom. The model is used to carry out a sensitivity analysis of the reacidification of a limed lake. Based on the dissolution models a neutralization dose calculation routine is suggested, defining a minimum required dose and a maximum dose. Costs of lake liming is discussed and the reacidification model used to carry out a sensitivity analysis of neutralization costs for lakes.				
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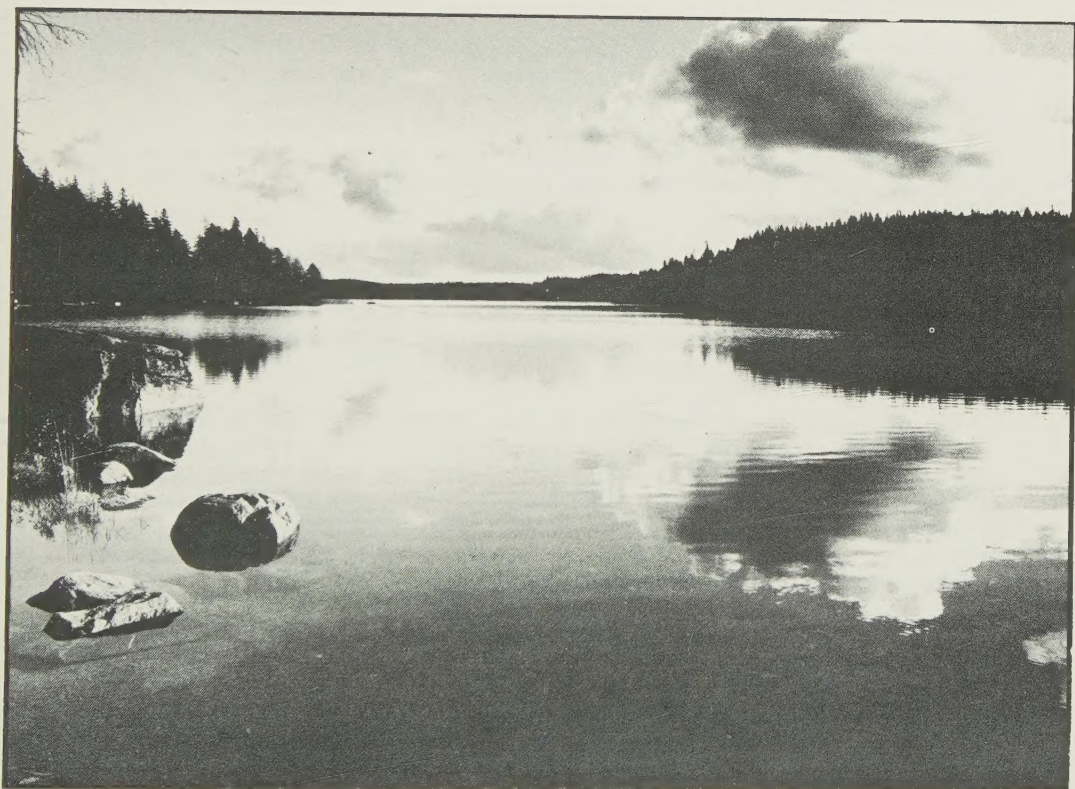
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I. INTRODUCTION



Introduction

In Sweden the first serious effects of acidification were detected on a larger scale in our lakes in the early 1960's. By then several decades of acidic deposition had changed the base saturation in the soils located on low weathering bedrock or mineral material and the runoff could no longer be completely neutralized during its passage through the soil profile.

Today some 20 thousand lakes of a total of 200 thousand lakes in Norway and Sweden will have a pH-value below pH 5.5 some time during the year. In several acidified regions such as the provinces of Agder in Norway or the provinces of Bohuslän and Småland as much as 50 % of all lakes and streams are affected. Every year more lakes and streams acidify as a consequence of continued cation depletion and acidification of the soil (SNV 1982, Baalsrud et al 1985).

In recent years signs of the most dreaded effect of acid deposition and soil acidification have been detected; forest growth rate reduction and forest die-back. The forest plays an important role in the Swedish national economy and forest die-back may seriously threaten the nations pulp and paper industry. Surveys are being carried out to estimate the exact effect of the problem and its development with time (SNV 1982).

The effects of acidification have also been shown to affect shallow aquifers and groundwater in areas where the mineral component of the soil is mostly granitic. This is the natural consequence of long term acidification and a growing problem. It causes corrosion problems to the traditional iron or copper water supply systems as well as causes damage to constructions (Jacks & Knutsson 1981, Levlin 1978).

Liming of lakes, streams or soil is in no way an acceptable solution to the acidification problem. Still it is the only large scale remedy for postponing some of the effects of acidification, until emissions of sulfurdioxide and nitric oxides in Europe have been reduced substantially (Monitor 1984).

Liming of lakes and streams and to some extent soil liming started 15 years ago, often initiated by local sportsfishing associations or interested individuals. By 1980, 1000 lakes had been limed. In small scale liming projects, cost efficiency was not crucial but today the situation is different. For the fiscal year 1985-1986, the Swedish Parliament has budgeted 90 million Swedish Kronor for acidification mitigation and research (\$10 million).

Objectives and scope

The large acidification mitigation program results in an increased demand for competent selection of objects to be considered as well as efficient administration and planning. Competent technical planning and adequate design and calculation routines are needed in order to be able to produce cost efficient liming operations.

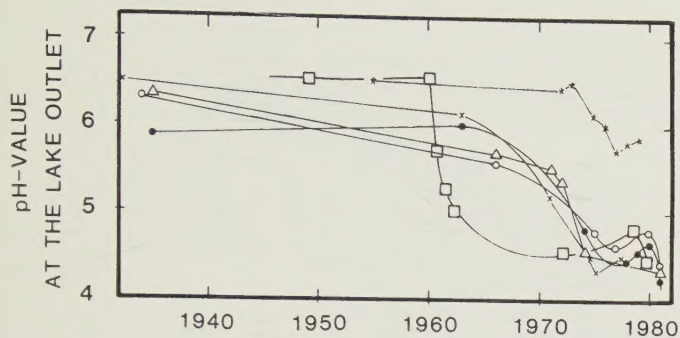


Figure 1a.

Acidification trends in some Swedish lakes located on low weathering granitic soils, and with small soil depth.

- Ålevatten, Stenungsund
- △ Ballasjön, Borås
- Enningen, Borås
- Vatthultasjön, Borås
- × Uppsälén, Borås

Lakes located in watersheds with larger soil depth may take more time to acidify:

- ★ Multen, Örebro

Source; Fiskerinämden i Borås, Fiskerikonsulent Sune Sander, Dr. Harald Alander, 1982

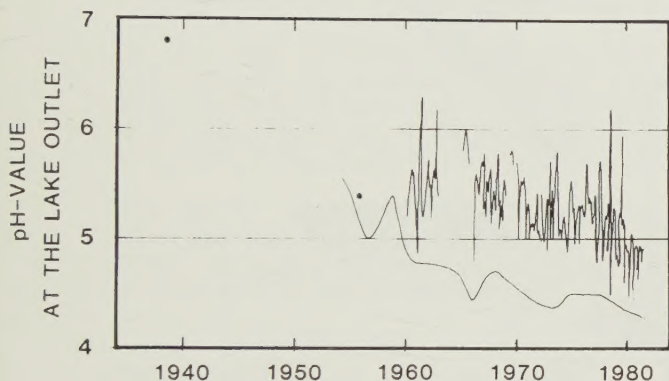


Figure 1b.

The pH-value at the outlet of lake Tjurken, a headwater lake in the Helgeå River system. The lower line indicates the pH-value of the precipitation in the Province of Småland, where the lake is located. The lake has a hydraulic retention time of 1.2-1.6 years. The lakes watershed consists of bogland and coniferous forrests on podsoles. Source; Vattenfalls Laxodling i Långhult, Göran Nennefors, 1982.

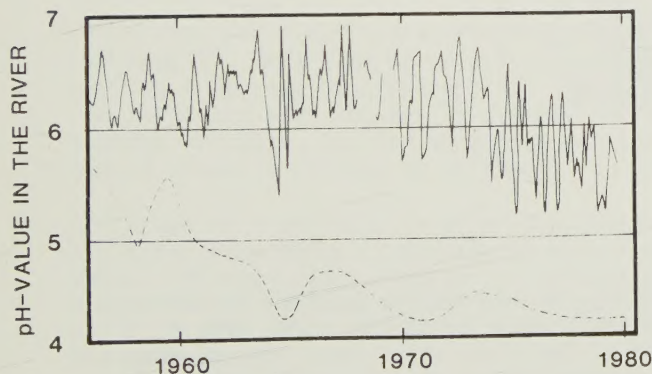


Figure 1c.

The pH-value in the Helgeå River at Delary Paper Mill. The very large watershed is characterized by thick glacial moraines of mostly granitic origin. Most of the watershed is covered by coniferous forrest on brown podsoles. Source; Delary Bruk, Södra Skog-ägarna, Lennart Öberg, 1982.



Figure 1d

Lakes in many regions of Norway and Sweden have become acidified. The shaded areas indicate where a majority of the lakes have a pH-value between pH 5 and pH 6. The black areas indicate regions where a majority of the lakes or streams have a pH-value below pH 5. The map was put together with information from Baalsrud et al. (1985) and Acidification Today and Tomorrow (1982)

With respect to the Swedish liming program, several areas of interest could be identified as areas where specific knowledge was needed and had to be developed:

- Kinetical expressions for the dissolution of calcite, describing the dissolution in aqueous solutions as a function of solution pH-value, mineral composition, particle size and other critical parameters.
- Models to predict the dissolution of a calcite powder in an acidic water column under condition prevailing during lake liming.
- Dose calculation routines, to calculate the actual dose to be applied as a function of water chemistry, particle size and required target concentrations of alkalinity and pH.
- Ways to predict the reacidification of a limed lake. A model should be able to predict the development of critical parameters such as pH, alkalinity or calcium concentration with time as well as any possible long term dissolution.
- Integration of the several sectors of knowledge into an overall acidification mitigation strategy.

The last item is indeed a large one, and goes beyond the scope of this work. It has however been dealt with elsewhere (Sverdrup et al 1983, Sverdrup & Warfvinge 1983, Sverdrup & Warfvinge 1984, Sverdrup et al 1984, Warfvinge & Sverdrup 1984, Sverdrup & Warfvinge 1985, Britt, De Pinto, Sverdrup & Warfvinge 1985).

This thesis is concerned with the dissolution of calcite in particular and how this knowledge may be used to develop engineering tools and models able to deal with different situations encountered in lake acidification mitigation.

Characterization of solid particles

It is necessary to define some important aspects of describing and handling of particulate solids before entering the topic of heterogeneous reactions and mineral particle dissolution kinetics.

Individual solid particles are characterized by their size, shape and density. Particles of relatively pure crushed minerals have a density which may be considered as constant in a crushed product. The shape and size are easily defined for regular particles such as spheres or cubes, but for irregular particles, such as crushed or ground minerals it must be defined.

The shape of a particle is often described with a parameter called the sphericity which is defined in relation to the equivalent diameter. The equivalent diameter is defined as the diameter of a sphere having the same volume as the particle. The sphericity is the ratio of this sphere's surface area to the actual surface area of the particle.

Neutralizing agents used for lake liming usually come as a powdered material, being a mixture of a large variety of particle sizes. Such a mixture is described with a particle size distribution.

For particles larger than 0.5 mm the particle size distribution is generally determined by dry sieving on metal screens. However, as the particles get smaller, very small particles in the micron range will agglomerate with the larger ones to a substantial degree. Accordingly, dry sieving gives dubious results for particles in the 0.2-0.5 mm range and pure nonsense for particles less than 0.2 mm.

All mineral powders used for lake liming contain a substantial amount of particles less than 0.2 mm, if not all. Only such particle size distributions which have been determined by wet sieving, sedigraph, laser determination or some otherwise equivalent method are acceptable. Screened fractions of particles for dissolution experiments will have to be prepared accordingly.

An example of particle size distributions is shown in figure 2 a and shows calcite powders sold on the Swedish market.

Two particle size distribution curves as obtained by wet sieving are shown in figure 2 b together with the size distribution curves for the same powders determined by dry sieving.

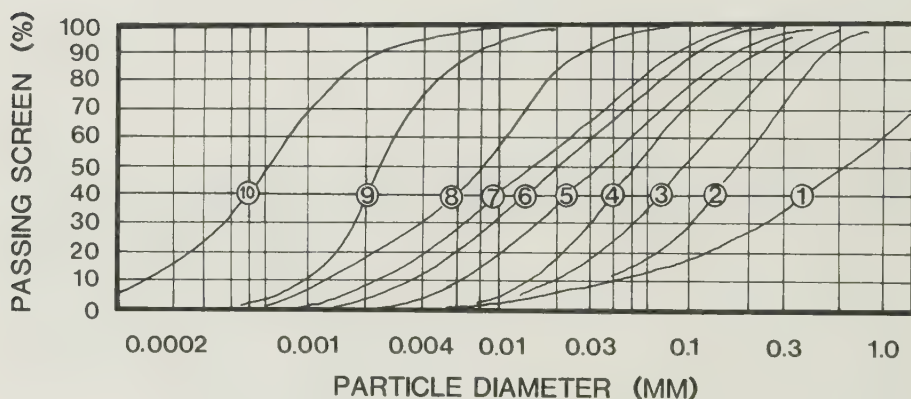


Figure 2a

An example of particle size distribution curves for powder used for liming in Sweden. They are generally sold under commercial names such as

- 1-2 0-3 mm Agricultural limestone
- 3-4 0-2 mm Agricultural limestone
- 5 0-1 mm Agricultural limestone
- 6 0-0.5 mm Calcite powder GG 250
- 7 0-0.2 mm, 0-0.250 mm, GG 100, 0-0.125 mm, 0-0.1 mm Calcite powder
- 8 0-0.044 mm, 0-0.05 mm, Mesa,
- 9 Chalk filler, Malmö chalk, Faxé chalk
- 10 Marble filler, Carbital, Hustad marble

The dissolution of minerals is proportional to the surface area of the mineral exposed to the solution. This surface area may be expressed as the specific area of the particle mixture in m^2 per kg mineral:

$$A_W = \frac{3}{\varphi \cdot \rho} \cdot \sum_{i=1}^n \left(\frac{\Delta \phi_i}{r_i} \right) \quad m^2/kg \quad (1)$$

where φ is the sphericity of the material, ρ particle density. The powder has been numerically divided into n classes of particle sizes and $\Delta \phi_i$ is the fraction of the particles having an average radius of r_i .

The average particle size for particle mixtures may be defined in several ways, based on diameter, number of particles, particle surface area as well as volume. For dissolution studies and liming the average particle size related to the surface area is of most interest. It is defined as:

$$r = \frac{3}{\varphi \cdot A_W \cdot \rho} \quad m^2 \quad (2)$$

For the minerals discussed in this text, the sphericity φ has a value of 0.85-0.95 for the minerals of crystalline form and a value of 0.75-0.90 for the sedimentary calcitic and dolomitic limestones. The density is virtually the same for all minerals studied and has been set at 2700 kg/m^3 .

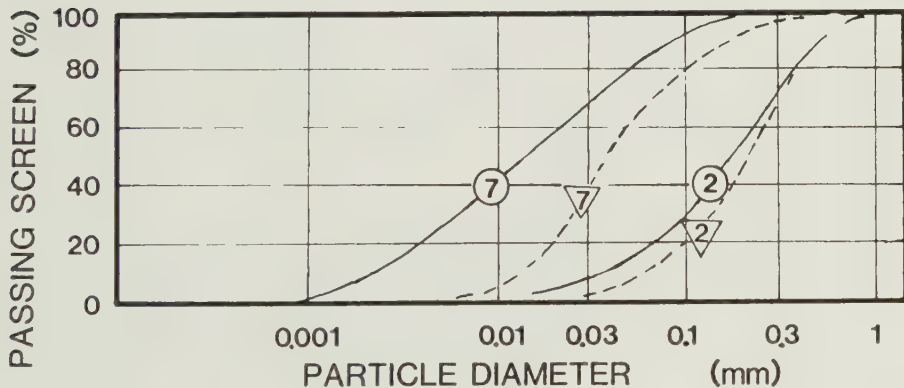


Figure 2b Comparison of a particle size distribution curve determined by sedigraph or wet sieving to a curve obtained by dry sieving on metal screens. For powders containing a large portion of particles smaller than 0.2 mm, the dry sieving gives wrong estimates, for particles in the range 0.2 mm - 0.5 mm the results are dubious.



CALCITE DISSOLUTION KINETICS AND LAKE NEUTRALIZATION

1. MINERAL DISSOLUTION KINETICS

The principles of solids dissolving in liquids

Consider a particle dissolving in an aqueous solution, acidic or circumneutral. Then several processes are taking place in series. First the substances that will react with the solid particle are transported from the bulk of the liquid down to the particle surface. On the surface they will react with the substance of the particle by one or more chemical reactions. If soluble, the products of the reaction will be transported back into the bulk of the liquid. Generally the mechanism of mass transfer between the solid particle surface and the bulk of the liquid will be molecular diffusion.

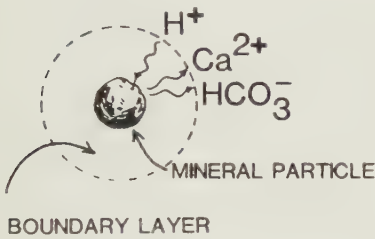


Figure 3

The dissolution occurs as a chemical reaction at the solid particle surface. For very fast reactions the diffusion of reactants through the boundary layer is the rate limiting step.

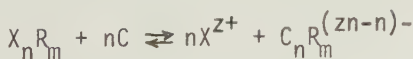
When a process takes place as a series of steps, all occurring at different rates, then the overall rate of progress for the process will be determined by the slowest step in the series.

If the rate of chemical reaction on the particle surface is slower than the transport of reactants to the surface by diffusion, then the overall reaction rate may be said to be kinetically controlled. If diffusion is the slower process, it is said to be diffusion controlled.

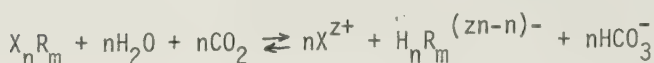
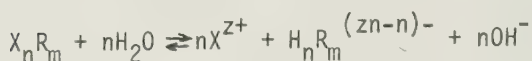
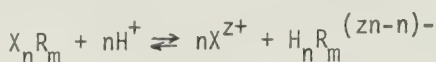
If it is assumed that the dissolution of a mineral particle is proportional to the surface area of each particle and that the dissolution proceeds with w forward reactions and v backward reactions, then the overall reaction rate is given by the sum of all forward reaction rates minus the sum of all backward reaction rates:

$$-\frac{dm}{dt} = \left[\sum_{j=1}^w K_j \cdot [C_j]^{n_j} - \sum_{i=1}^v K_{B_i} \cdot [X_i]^{y_i} \cdot [R_i]^{z_i} \right] \cdot A_s \quad (3)$$

for a congruent dissolution of a mineral:

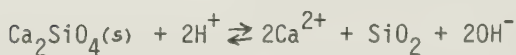
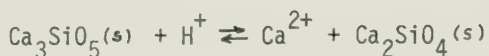


where k_j is the forward rate for reaction j between C_j and the solid, with reaction order n . K_{Bj} is the backward reaction rate dependent on the reaction product X and R . A_s is the specific mineral surface area per mineral weight. Most minerals will react with the hydrogen ion, carbondioxide and the water itself in an aqueous solution. The reactions will be of the following type, while X is the cation and R the anion:



$[C_j]$ in the expression represents the concentration of the reacting species in the solution.

Several minerals undergo incongruent dissolution, as dolomite or tricalciumsilicate:



The reaction order for a congruent reaction will be determined by the stoichiometry of the rate limiting reaction. However, for incongruent dissolution the reaction order cannot be apriori deduced in a simple way. Incongruent dissolution may involve many mechanisms and the order of reaction may change with time (Helgeson et al, 1971).

In a mass m of particles of uniform radius; r , the specific mineral surface area will be given by

$$A_s = \frac{3 \cdot m}{\rho \cdot r} \quad m^2 \quad (4)$$

The dissolution rate for most minerals may often be described by an expression of the type:

$$-\frac{dm}{dt} = (K_1 \cdot [H^+]^n + K_2 \cdot [CO_2]^m + KW - KB \cdot [X]^y \cdot [R]^z) \cdot \frac{3 \cdot m}{\rho \cdot r} \quad (5)$$

As water is indeed abundant in dilute aqueous solutions, the reaction with water may generally be regarded as a reaction of zero order, and it may be represented by a constant KW .

For kinetically controlled dissolution processes the rate constants of eq. 3 will be true rate constants, variable with the temperature only.

Experience from dissolution of minerals (Sverdrup & Bjerle 1982) has shown that the reaction with the hydrogen ion usually determines the overall reaction rate at lower pH-values in the solution.

Assuming that the reaction with the hydrogen ion is diffusion controlled and the other reactions kinetically controlled, as for calcite, we could write the expression for the dissolution of a mineral due to the reaction with the hydrogen ion:

$$-\frac{dm}{dt} = D \cdot \left(\frac{\partial [H^+]}{\partial r} \right)_p \cdot \frac{3 \cdot m}{\rho \cdot r} \quad \text{kmol/s} \quad (6)$$

$(\partial [H^+]/\partial r)_p$ is the gradient of the hydrogen ion concentration at the particle surface. The gradient around a spherical particle is given by the classical diffusion equation, expressed in spherical coordinates:

$$\frac{\partial [H^+]}{\partial t} = D \cdot \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left(r^2 \left(\frac{\partial [H^+]}{\partial r} \right) \right) \quad \text{kmol/m}^3 \text{ s} \quad (7)$$

By assuming pseudo-steady-state in the boundary layer and using the conditions in the bulk of the liquid and at the particle surface as boundary conditions, the equation may be solved with respect to the gradient desired. The general solution is:

$$\frac{\partial [H^+]}{\partial r} = [H^+] - [H^+]_p \left(\frac{r_p + \Delta r}{r \cdot \Delta r} \right) \quad \text{kmol/m}^4 \quad (8)$$

In this expression $[H^+]$ is the concentration of the hydrogen ion in the bulk of the liquid, $[H^+]_p$ the concentration at the particle surface. As the chemical rate on the particle surface is very much faster than the diffusion rate, then the hydrogen ion concentration may be considered to be virtually zero as compared to the concentration in the bulk of the liquid. Hence we may put:

$$[H^+] = [H^+] - [H^+]_p \quad [H^+] \gg [H^+]_p \quad (9)$$

Δr is the boundary layer around the particle, a region of stagnant solution. In stirred systems Δr is typically 10-30 μm . The boundary layer thickness may be calculated with semiempirical relations as given by Sherwood et al (1975).

In stirred systems we get for particles larger than 10 μm in diameter

$$D = \left(\frac{1}{\Delta r} + \frac{1}{r} \right) \longrightarrow D/\Delta r \quad \text{m/s} \quad (10)$$

For particles less than 10 μm and for all stagnant systems regardless of particle size, the rate coefficient becomes:

$$D = \left(\frac{1}{\Delta r} + \frac{1}{r} \right) \longrightarrow D/r \quad \text{m/s} \quad (11)$$

as the boundary layer thickness is approaching infinity in stagnant systems $\Delta r \gg r$.

For the dissolution of a mineral at very low pH-values, below pH 4.5, the reaction with the hydrogen ion usually dominates. For such a situation the kinetical expression may be simplified to become

$$-\frac{dm}{dt} = D \left(\frac{1}{r} + \frac{1}{r} \right) \cdot [H^+] \cdot \frac{3 \cdot m}{\rho \cdot r} \quad \text{kmol/s} \quad (12)$$

if the process is diffusion controlled.

This may be compared with the expression obtained if the process is kinetically controlled:

$$-\frac{dm}{dt} = K_1 \cdot [H^+]^n \cdot \frac{3 \cdot m}{\rho \cdot r} \quad \text{kmol/s} \quad (13)$$

It can be seen that if the dissolution of a mineral is diffusion controlled with respect to the hydrogen ion, then the order of reaction must be one; $n = 1.0$. If the reaction order to be expected of a kinetically controlled process is different from $n = 1.0$, we may easily determine if the dissolution of the mineral is kinetically controlled or diffusion controlled.

If the reaction order is experimentally determined to be $n = 1.0$ and the order of reaction to be expected in a kinetically controlled process is $n = 1.0$, then it would be possible to distinguish diffusion control from kinetic control by studying the dissolution of particles smaller than 10 microns. If the reaction is diffusion controlled it will be proportional to the inverse of the particle size squared, but only proportional to the inverse of the particle size if the reaction is kinetically controlled.

By plotting the logarithm of the dissolution rate versus pH we may estimate n as the slope of the curve and the intercept at $\text{pH} = 0$ will give the value of $\log K$:

$$\log \left(-\frac{dm}{dt} \cdot \frac{\rho \cdot r}{3 \cdot m} \right) = n \cdot \text{pH} + \log K_1 \quad (14)$$

For diffusion controlled reactions K would be equal to D/r for stagnant systems or particles less than 10 microns and $D/\Delta r$ for particles larger than 10 microns.

The backward reaction rate

If it is assumed that the dissolution of the minerals of interest may be described with an expression such as eq 3. By substituting the variables with:

$$r = r_0 \left(\frac{m}{m_0} \right)^{1/3} \quad (15)$$

eq. 3 may be integrated, giving the solution for kinetically controlled reactions and for diffusion controlled reactions on particles larger than $10 \mu\text{m}$ in a stirred solution:

$$1 - (m/m_0)^{1/3} = \left(K_1 \cdot [H^+]^n + K_W - K_B \cdot [X]^y \cdot [R]^z \right) \cdot \frac{t}{\rho \cdot r_0} \quad (16)$$

Here we have limited ourselves to such systems where the reaction with carbondioxide may be neglected. That is the case for calcite dissolution in natural waters such as lakes or streams.

In a plot of $1-(m/m_0)^{1/3}$ versus the time t , a straight line should be expected if all concentrations were constant in the solution. In a pH-stat controlled experiment, the hydrogen ion concentration is kept constant, but the concentration of reaction products will steadily rise as the experiment proceeds. The curve will accordingly bend off from the straight line as the backward reaction rate increases with rising reaction product concentration.

Determine the slope α in the expression

$$1 - (m/m_0)^{1/3} = \alpha \frac{t}{\rho \cdot r_0} \quad (17)$$

at the start of the experiment ($t = 0$). This slope we will call α_0 ;

$$\alpha_0 = K_1 \cdot [H^+]^n + KW \quad \text{kmol/m}^2 \text{ s} \quad (18)$$

At any other point in time during the experiment, when the reaction product concentration is not equal to zero, the slope is given by α_t .

$$\alpha_t = K_1 \cdot [H^+]^n + KW - KB \cdot [X]^y \cdot [R]^z \quad \text{kmol/m}^2 \text{ s} \quad (19)$$

where $[X]$ and $[R]$ are the concentration of the products of reaction at the time t . By subtracting the initial slope at $t = 0$ and the slope at some later time, we obtain

$$\alpha_0 - \alpha_t = KB \cdot [X]^y \cdot [R]^z \quad \text{kmol/m}^2 \text{ s} \quad (20)$$

By plotting $\log (\alpha_0 - \alpha_t)$ versus $\log [R]$ the order of reaction with respect to species R may be determined, as the slope of the curve.

$$\log (\alpha_0 - \alpha_t) = z \cdot \log [R] + \log \beta \quad (21)$$

The intercept at $\log [R]_t = 0$ will give the number $\log \beta$ which equals:

$$\log \beta = y \cdot \log [X] + \log KB \quad (22)$$

If the experiments are carried out in different solutions which initially contain X but no R the expression for the dissolution is still valid and we may determine a set of values for β corresponding to a set of different concentrations of X.

By plotting $\log \beta$ versus $\log [X]_{t=t}$ the reaction order y may be obtained as the slope of the curve and $\log KB$ as the intercept at $\log [X]_{t=t} = 0$.

Chemical reactions and kinetic expressions

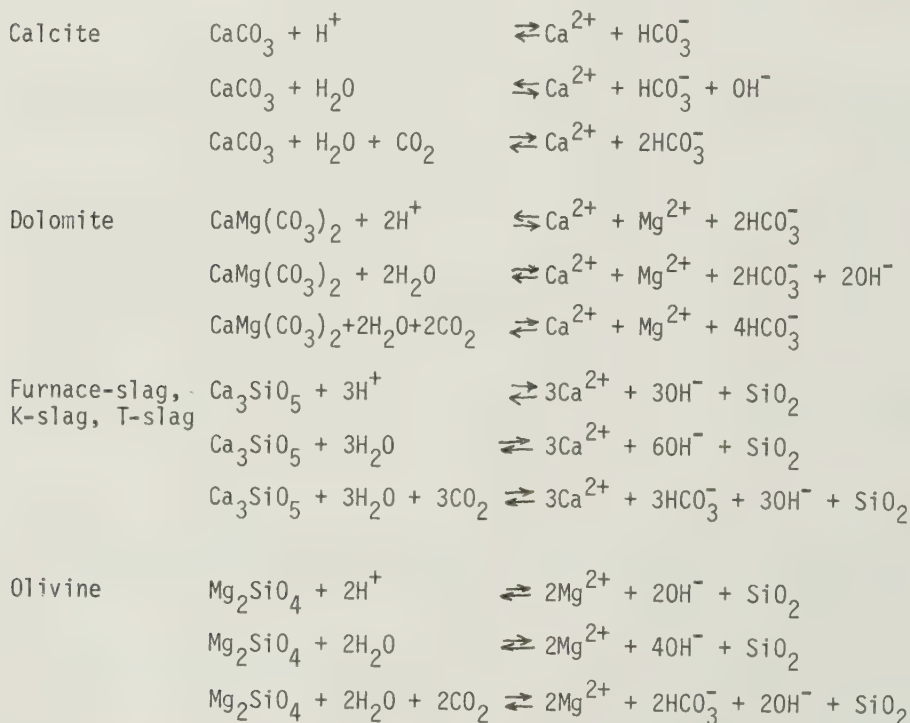
The dissolution kinetics were determined for a number of minerals and some few industrial chemicals. The experiments were carried out in a pH-stat, an apparatus designed to keep the hydrogen ion concentration constant in a reaction vessel. It consists of an autoburette, automatic titrator and a pH-meter and a chart recorder.

The pH-stat keeps the pH-value constant in a reaction vessel during experiments. Dissolving mineral will consume hydrogen ions which are replaced by the apparatus and the added amount is recorded. Accordingly a continuous curve of mass consumed with time is obtained.

The experiments were carried out with dilute sulfuric acid, at low salt concentrations and at 25°C.

With the pH-stat the dissolution kinetics was determined and the specific rate constants estimated for carbonate minerals such as sodiumcarbonate, calcite, dolomite, as well as other minerals, olivine, tricalciumsilicate, cementclinker, slaked lime and sodium hydroxide.

The most important chemical reactions involved in dissolution are:



The kinetic expression for calcite could be determined to be:

$$-\frac{dm}{dt} = \left(\frac{D}{\Delta r} \cdot [\text{H}^+] + K_2[\text{CO}_2] + K_W - K_B \cdot [\text{Ca}^{2+}][\text{HCO}_3^-] \right) \cdot \frac{3 \cdot m}{\rho \cdot r} \quad (23)$$

for particles larger than 10 microns in stirred aqueous solution.

For particles smaller than 10 microns, and for all particles under stagnant conditions:

$$-\frac{dm}{dt} = \left(\frac{D}{r} \cdot [H^+] + K_2[CO_2] + KW - KB \cdot [Ca^{2+}][HCO_3^-] \right) \cdot \frac{3 \cdot m}{\rho \cdot r} \quad (24)$$

The mass transfer coefficient in eq. 23, $K_1 = D/\Delta r$ may be estimated with a relation called the Frössling-equation (Sherwood et al, 1975):

$$K_1 = \frac{D}{r} (1 + 0.3 \cdot Re^{1/2} \cdot Sc^{1/3}) \quad m/s \quad (25)$$

The rate for the carbondioxide reaction was not actually measured, as this work only concerned waters free of carbondioxide or in equilibrium with air. Plummer et al (1978) investigated the dissolution of calcite under different carbondioxide pressures and found that the reaction with carbondioxide has no significant effect on the overall rate at partial pressures less than 0.1 atm.

Carbondioxide partial pressures in excess of 0.1 atm do never occur in open systems such as lakes or strams, nor in shallow aquifers (Hutchinson 1975, Bouten et al, 1984).

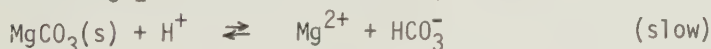
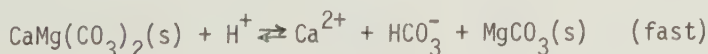
Eq. 22 implies that particles of different size will react differently to the hydrogen ion concentration. For particles approximately 10-20 microns in diameter the reaction with the hydrogen ion will be the dominating process below pH 5.5. For particles with a diameter of 100-200 microns in stagnant media the hydrogen ion reaction will be dominant at pH-values below pH 4.5, whereas for very small particles; 1-2 microns, the reaction with the hydrogen ion will dominate at pH-values below pH 6.5.

The dissolution of calcite is rather insensible to the origin of the stone as a consequence of the fact that the dominating process is diffusion controlled. The diffusion is determined by the concentrations in the solution and does not "feel" the origin of the stone. However, contents of magnesite in the stone will be able to lower the dissolution rate substantially.

For dolomite the expression becomes

$$-\frac{dm}{dt} = \left(K_1 \cdot [H^+]^{1/2} + K_2[CO_2]^{1/2} + KW - KB \cdot [HCO_3^-] \right) \cdot \frac{3 \cdot m}{\rho \cdot r} \quad (26)$$

The order of reaction arises from the fact that dolomite dissolves incongruently. This implies that the calcium component dissolves more easily than the magnesium component the reaction occurs in two steps:

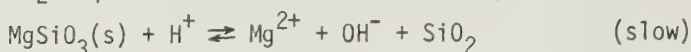
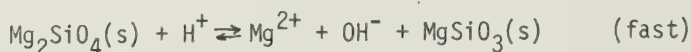


Accordingly the dissolution rate will be dependent on only half the total amount of reactants consumed per mole of solid dissolved, this may cause the order of reaction to equal to one half (Busenberger et al 1982).

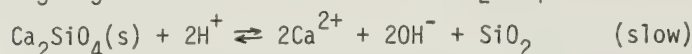
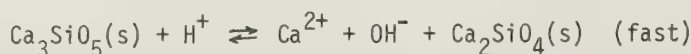
The kinetics of several silicates were determined as well, such as olivine or forsterite:

$$-\frac{dm}{dt} = (K_1 \cdot [H^+] + K_W - K_B \cdot [SiO_2]) \cdot \frac{3 \cdot m}{\rho \cdot r} \quad \text{kmol/s} \quad (27)$$

Olivine dissolves incongruently and follows several mechanisms. The limiting factor may be the dissolution of $MgSiO$ or enstatite after the forsterite has been leached of magnesium ions (Luce et al 1975);



K-slag is the commercial name of a blast furnace slag and it has been used to some extent as a substitute for agricultural limestone. It is a tricalcium silicate and it dissolves incongruently in water:



As the reaction is dependent on two thirds of the total amount of reactant per mole solid consumed the order of reaction could be two thirds. The kinetic expression could be determined to be

$$-\frac{dm}{dt} = (K_1 \cdot [H^+]^{2/3} + K_W - K_B \cdot [SiO_2]^{1/3}) \cdot \frac{3 \cdot m}{\rho \cdot r} \quad (28)$$

The backward reaction acts quite strongly even at fairly low concentrations of silicate and accordingly at the concentration of silicate rises, the dissolution rate declines rapidly.

Cementclinker is another calcium-aluminium silicate produced as a raw product for cement manufacture. It dissolves incongruently and the kinetic expression for the forward rate is:

$$-\frac{dm}{dt} = (K_1 \cdot [H^+]^{1/6} + K_W - \dots) \cdot \frac{3 \cdot m}{\rho \cdot r} \quad \text{kmol/s} \quad (29)$$

The backward rate was not determined for cementclinker.

The dissolution of K-feldspar is a complicated process, involving several stages of diffusion in the solid crystal after an initial phase with surface ion exchange. However for long term weathering of feldspar by acid solutions, a simple expression may serve as an approximation:

$$-\frac{dm}{dt} = (K_1 \cdot [H^+] + K_W - K_B \cdot [SiO_2]) \cdot \frac{3 \cdot m}{\rho \cdot r} \quad (30)$$

Only K₁ and K_W were determined and included in this study in order to provide data for a very slowly dissolving mineral for comparison.

The dissolution of solid particles of industrial chemicals such as slaked lime or soda ash, is very rapid and they will generally dissolve completely when used in liming operations.

The dissolution of slaked lime in hydrochloric acid is of reaction order zero with respect to the hydrogen ion, but in dilute sulfuric acid it is substantially slower and of order 1/4 with respect to the hydrogen ion:

$$-\frac{dm}{dt} = K_1 \cdot [H^+]^{1/4} \cdot \frac{3 \cdot m}{\rho \cdot r} \quad (31)$$

The dissolution of sodium carbonate and sodium hydroxide is of reaction order zero, and very rapid:

$$-\frac{dm}{dt} = \frac{3 \cdot m \cdot K_W}{\rho \cdot r} \quad (32)$$

The backward reaction rate was not measured for these chemicals.

Rate constants

The actual numerical value of the determined rate constants are listed in table 1. The listed values are the logarithm of the rate based on a dissolution rate expressed as kmol/s. The rate constant for calcite particles in a stagnant system will be dependent on the particle size as mentioned earlier:

$$K_1 = \frac{D}{r} \quad (33)$$

For stirred systems with particles smaller than 10 microns the relation above is valid but for larger particles it is given by

$$K_1 = \frac{D}{\Delta r} \quad (34)$$

where Δr is fairly constant throughout a wide range of particle sizes.

The expression gives the mass transfer coefficient due to diffusion into a sphere falling in a liquid at its terminal velocity. The observed K₁'s for calcite dissolution were plotted in a diagram versus the particle diameter together with the Frössling equation, using the diffusion coefficient D for the hydrogen ion. The diagram is shown in figure 4. In the calculations D was assigned the value; $D = 1 \cdot 10^{-8} \text{ m}^2/\text{s}$. The correspondence between the Frössling equation and the observed values confirms that the reaction of calcite with the hydrogen ion is indeed diffusion controlled.

Mineral	Formula	pK1	pKW	pKB	pK2
Calcite	CaCO_3	- 3.0	- 8.9	-2.4	-6.7
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	- 6.8	-10.5	-7.2	-9.3
Olivine	Mg_2SiO_4	- 6.5	-13.0	-	-
K-slag	Ca_3SiO_5	- 6.5	- 7.85	-7.0	-
K-feldspar	KAlSi_3O_8	-11.5	-16.7	-	-
Cementclinker	-	-7.0	- 7.9	-4.2	-
Slaked lime	$\text{Ca}(\text{OH})_2$	-3.3	-	-	-
Sodium carbonate	Na_2CO_3		- 0.8	-	-
Sodium hydroxide	NaOH		- 0.2		

Table 1 The rate constant values for the dissolution of some minerals. The value for the reaction of calcite with the hydrogen ion applies to particles in stirred solutions when the particles are larger than 10 microns. The values were obtained from experiments by the author of from the literature (Dolomite pK2 and pKB, Busenberger et al 1982, K-feldspar pK1, pK2, pKW, pKB Helgeson et al 1971). A bar indicates that the value was not determined (-) and an empty space that the coefficient does not exist.

Origin	$K_1 \cdot 10^3$	φ	$K_1 \cdot \varphi \cdot 10^3$	Crystal form
Köping, Södermanland	(0.98 ⁺ 0.07)	0.90	0.88	Crystalline
Storugn, Gotland	(1.00 ⁺ 0.12)	0.90	0.90	Metamorph rock
Ignaberga, Skåne	(1.24 ⁺ 0.08)	0.75	0.93	Agglomerated shells
Limhamn, Skåne	(1.05 ⁺ 0.04)	0.85	0.89	Chalk

Table 2 The geological origin of the mineral and its crystal structure is without influence on the reaction of calcite with the hydrogen ion. Four different calcites of Swedish origin were used for repeated dissolution experiments and the rate for the reaction with the hydrogen ion was determined

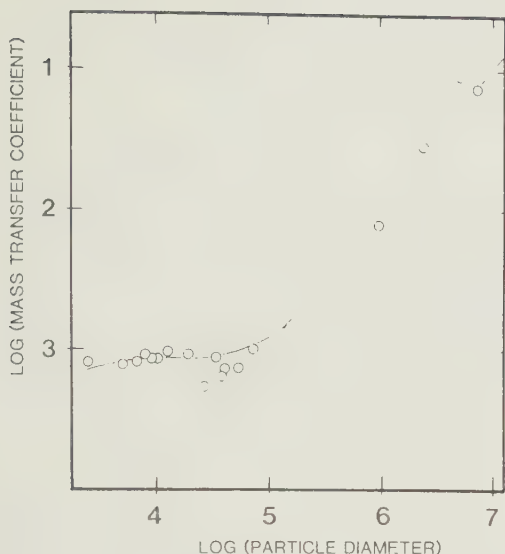


Figure 4

The observed mass transfer coefficient from dissolution experiments with calcite as compared to the predicted values by the Frössling expression.

For calcite particles in the size range 10-200 microns, $-pK_1$ has a value of approximately 2.9-3.2 for calcite.

The dissolution rates per time and specific mineral surface area for a number of chemicals and minerals are plotted versus pH in figure 5. K-feldspar, the typical mineral constituent of soils that cannot withstand the acidification, is incorporated for comparison.

Calcite dissolution rate varies very little with the temperature whereas the kinetically controlled reactions of such minerals as dolomite or olivine may vary substantially.

Minerals of different geological origin

The dissolution rate will not be affected by the origin of the mineral or its crystalline structure if the reaction rate is diffusion controlled. The reaction of calcite with the hydrogen ion is diffusion controlled, and the dissolution of calcite at pH-values below pH 6.0 is accordingly independent of the origin of the mineral. This may be seen in the results from dissolution experiments with different Swedish calcites. The results are shown in table 2. If the observed values for the rate of reaction with the hydrogen ion are corrected for differences in sphericity, the values become very consistent and do not vary more than ± 3 percent. This is well inside the limits for experimental errors.

Depending on their molecular mechanisms, kinetically controlled dissolution reactions may be dependent on the origin of the mineral and its crystal structure. This has been shown clearly for the case of dolomite by Busenberger et al (1982).

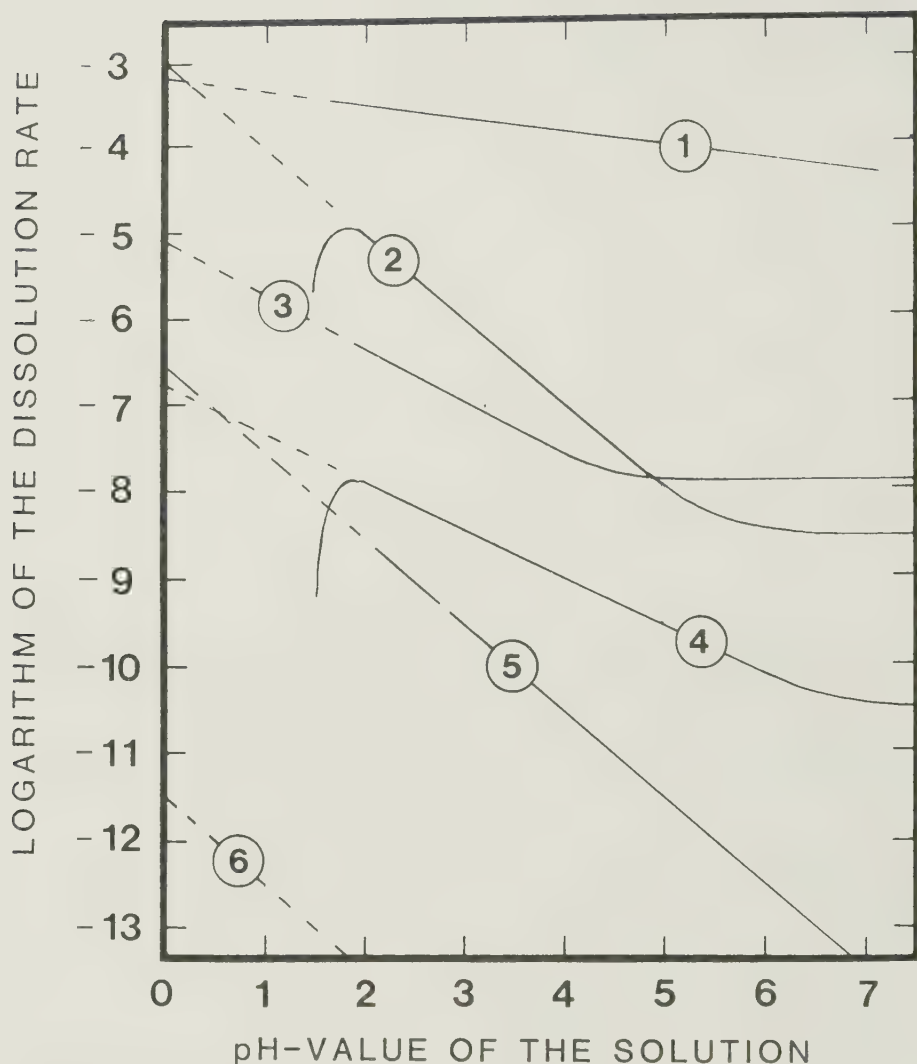


Figure 5

The dissolution rate for several minerals expressed as $\text{kmol/m}^2\text{s}$ versus the solution pH-value. The lines represent 1: Slaked lime in sulfuric acid, 2: Calcite, 3: K-slag or tricalciumsilicate, 4: Dolomite, 5: Olivine, 6: K-feldspar. The dissolution rate in sulfuric acid for all the carbonate minerals investigated were greatly reduced at low pH-values. The rate starts to fall off at pH 2 and it is virtually nil at pH 1.4. This is probably due to sulfate precipitation on the mineral surface. The effect of sulfate precipitation may be accounted for in the model by adding an extra backward term. The diagram is assembled with data from Sverdrup & Bjerle (1981), Sverdrup & Warfvinge (1985), Plummer et al (1978), Busenberger et al (1982), Helgeson et al (1971).

2. CALCITE DISSOLUTION KINETICS AND LAKE NEUTRALIZATION

Introduction

Lakes are usually neutralized by distributing a finely ground calcite powder over the lake surface area. Depending on the grinding grade as well as other parameters the powder may dissolve completely or partially. In order to design neutralization operations properly and be able to predict the outcome the fraction dissolved of the powder added must be known. On the bottom, the dissolution rate will be several orders of magnitude smaller than in the water column and the dissolution from the bottom will not be able to influence the establishment of a neutralized state significantly.

The model

When a calcite powder is spread in a lake, the particles will rapidly be distributed according to size, sink through the water column and dissolve simultaneously. Figure 6 shows a visualization of the concept. The dissolution process is controlled by the diffusion of hydrogen ions to the calcite particle surface at pH-values below pH 6.0. For pH-values above pH 6.0 the reaction with water will contribute significantly to the overall dissolution rate.

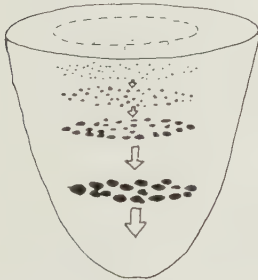


Figure 6

Vizualization of the sinking-dissolving lake liming model.

In this model the larger particles will sink more rapidly than the finer ones and as each size sinks it will dissolve and partially neutralize the water in its wake in front of the particles sinking slower.

By combining the dissolution kinetics for calcite with the Stokes equation for sinking particles an expression for a single sinking-dissolving particle may be derived as function of sinking depth:

$$-\frac{dm}{ds} = \left(\frac{27 \cdot \mu \cdot M_E \cdot m_0}{2 \rho_p (\rho_p - \rho_w) g} \right) \left(\frac{K_1 [H^+] + K_W}{r_0^3} \right) \quad (35)$$

If a powder composed of many different particle sizes and sinking through the water column as shown in figure 6 the following differential equation may be derived. A is a combination of various constants.

$$A = (27 \cdot \mu \cdot M_E \cdot m_0) / (2 \cdot \rho_p (\rho_p - \rho_w) \cdot g) \quad (36)$$

and for the dissolution of a calcite powder:

$$-\frac{d}{ds} \left(\sum_{i=1}^n m_i \right) = A \cdot \sum_{i=1}^n \frac{\Delta \phi_i}{r_{0i}^3} \left((K_1 \cdot [H^+] + KW) - \sum_{j=i-1}^{n-1} \left(\frac{m_0 - m_j}{A_L \cdot P \cdot M_E} \right) \right) \quad (37)$$

We define the dissolved fraction as X:

$$X = 1 - \left(\frac{1}{m_0} \cdot \left(\sum_{i=1}^n m_i \right) \right) \quad (38)$$

The differential equation may be analytically solved to yield

$$X = A' \cdot ((K_1[H^+] + KW) \cdot S \cdot \sum_{i=1}^n \left(\frac{\Delta \phi_i}{r_{0i}^3} (1 - P_i(B)) \right)) \quad (39)$$

where $A' = A/M_0$ and $P_i(B)$ is a polynominal given by

$$P_n(B) = \left(1 - \sum_{k=0}^{n-1} k \right) \cdot B + \left(1 + \sum_{k=0}^{n-2} \left(\sum_{k=0}^{n-1} k \right) \right) \cdot B^2 - \dots \quad (40)$$

$$+ (-1)^n \cdot \left(1 + \sum_{k=0}^1 \dots \left(\sum_{k=0}^{n-2} \left(\sum_{k=0}^{n-1} k \right) \right) \dots \right) \cdot B^n$$

B is a factor accounting for three properties; the mass transfer coefficient, the kinematic viscosity of the liquid and the dose of calcite.

$$B = \left(\frac{27 \cdot \mu}{2 \cdot \rho_p (\rho_p - \rho_w) \cdot g} \right) \cdot (K_1) \cdot \left(\frac{m_0}{A_L \cdot P} \right) \quad (41)$$

The dose is by far the most important component of the factor B. It is influenced by the design of the neutralization operation and it may vary quite much between different situations whereas the others remain more or less constant.

The above equations apply to particles larger than 10 microns. Smaller particles will dissolve substantially faster. Then K_1 is dependent on the particle diameter and the equation becomes more difficult to solve analytically.

However if numerical methods are used these difficulties are avoided and the dissolved fraction may be calculated for any conditions.

A calculation for the dissolved fraction is shown in figure 7 a. For the calculation it was assumed that the dose was modest, less than 30 g/m³ and that the dissolution was dependent on the reaction with the hydrogen ion and the reaction with water. The lake depth used in the calculation was 5 meter.

It can be seen from the analytical solution the differential equation that the dissolved fraction depends on the concentration of hydrogen ions and the depth in the same way:

$$X \propto [H^+] \cdot S \quad (42)$$

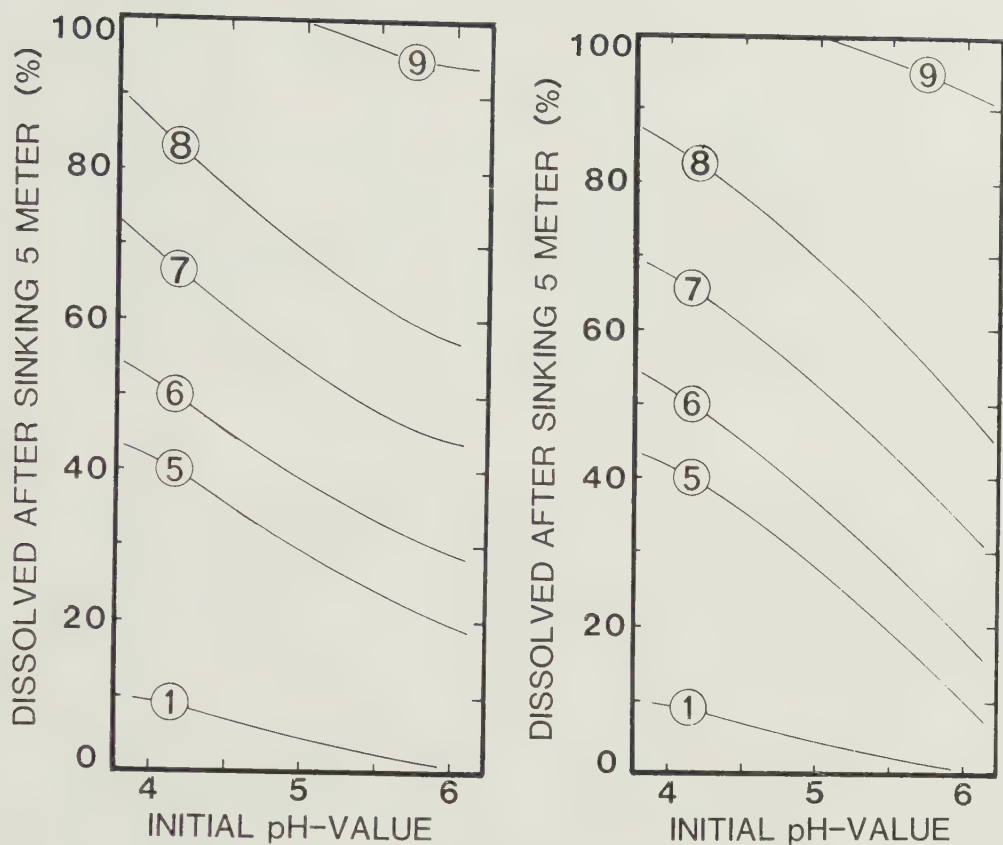


Figure 7a Dissolution curves for different calcite powders sinking in acidic water. It is assumed that the powder is applied well slurried in water. The number on the curves correspond to the particle size distribution curves shown in figure 2a.

Figure 7b The dissolution curves for different calcite powders when it is assumed that the dissolution is dependent on the reaction with the hydrogen ion only.

Accordingly a change in the lake depth S may be compensated for by changing the pH of the diagram correspondingly:

$$\text{pH}(\text{diagram}) = \text{pH}(\text{lake}) - \log \left(\frac{\text{actual depth}}{\text{five meter}} \right) \quad (43)$$

The formula is only applicable to the pH-region where the reaction with the hydrogen ion is prevalent. That applies for values of pH(diagram) less than pH 5.5.

For values of pH(diagram) larger than pH 5.5, the diagram deriving from a calculation where only the hydrogen-reaction term is considered must be used. Such a diagram is shown in figure 7 b.

In the diagram, a part of the analytical solution is shown; the part that applies to small dosages:

$$X = A' \cdot [H^+] \cdot S \cdot \sum_{i=1}^n \left(\frac{\Delta \phi_i}{r_{oi}^3} \right)$$

For larger dosages the full solution must be used and then an assisting diagram may be used. At higher dosages the dissolved fraction determined with the diagram in figure 7 a, is multiplied with a reduction factor RX

$$X(\text{Actual}) = X : RX \quad (44)$$

where RX is given by

$$RX = \left[\sum_{i=1}^n \left(\frac{\Delta \phi_i}{r_{oi}^3} \right) / \left(\sum_{i=1}^n \left(\frac{\Delta \phi_i}{r_{oi}^3} \right) (1 - P_i(B)) \right) \right] \quad (45)$$

RX is given as a function of the dosage in g/m^3 in figure 8.

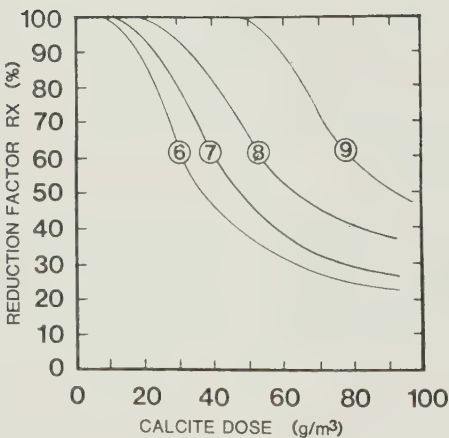
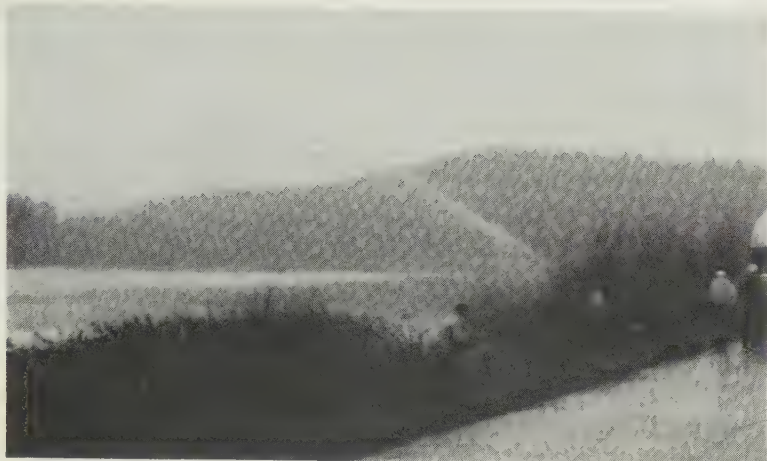


Figure 8

The figure shows the factor Rx by which the calculated dissolved fraction must be reduced by, as a result of overdosing. The diagram was experimentally determined for powder no.7 and no.9. The other lines are extrapolations aided by theory.



By applying the calcite powder as a well prepared slurry, a dissolution efficiency close to the theoretical maximum is achieved, as well as simplifies the application operation. Dry application generally creates a large dustbowl, which can be of considerable inconvenience to the workers as well as to the surroundings.

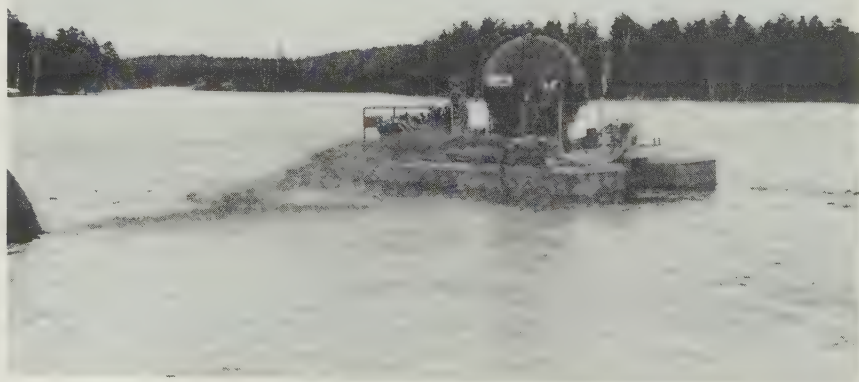
Application from a truck on the lakeside as shown in the picture, is a very inefficient method for neutralizing lakes. A very small fraction of the lake surface area is covered, often with a large dose, and the sinking depth is small in the littoral zone.

Application in the littoral zone has a function as a measure to prepare special habitats for spawning fish and such. However the effect of wave action on residual calcite in the littoral zone has been greatly exaggerated. The earlier assumptions have generally been based on datasets which does not contain the necessary information to decide the case. (Bengtsson et al.1981, Wright, 1982, Hultberg & Andersson, 1982) The sometimes very intensive wish for wave action on residual calcite in the littoral zone to be important, does not in any way prove that it works that way in reality.

Laboratory test

The model was tested against simulated lake limings in a 5 meter deep test tube containing artificial acid lake water. Two different powders were used at different initial pH-values as well as different dosages. The results indicate that when the powder is well slurried in water prior to application, then the model describes the observed dissolution with good accuracy. The result of the experiments are compared with the predictions of the theory in figure 7 c. The drawn line indicates the prediction obtained when the full expression for the dissolution rate is used. The dotted line indicates the prediction obtained when only the reaction with the hydrogen ion is considered.

The degree of wet slurring has a profound effect on the dissolution for lake liming. In a dry powder the particles will tend to aggregate and if these aggregates are not separated by wet slurring prior to liming they will be maintained as the powder sinks. The effect may be seen in figure 7 d where the results of two tests in the lake liming simulation tube are shown. The upper line and points repre-



The usual way to neutralize lakes is to distribute the powder from a barge carrying a 7 ton calcite supply. The powder is well mixed before spreading. Such an equipment will generally be able to distribute 5-10 ton per hour.

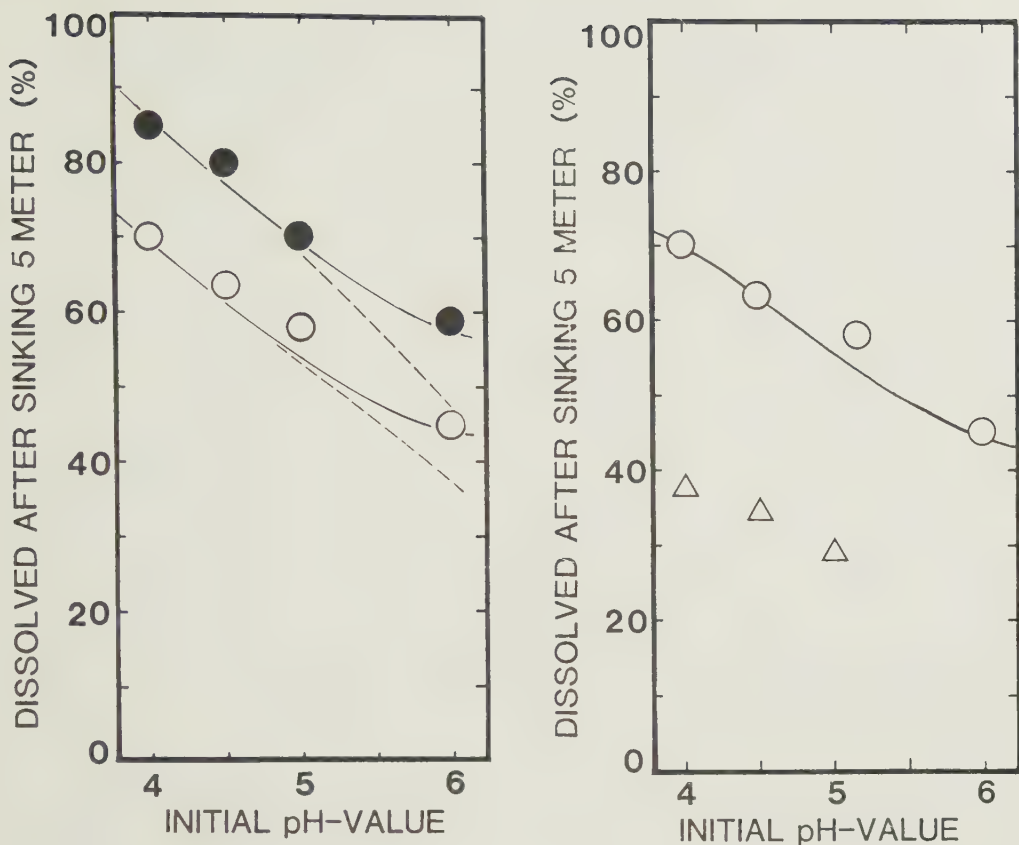


Figure 7c

The dissolution model was tested in a lake liming simulator, a 5 meter deep tank filled with sulfuric acid. The black dots (•) represent the observed values for powder no. 8, the drawn line the prediction of the model. The dotted line shows the prediction obtained if it is assumed that the dissolution is dependent on the hydrogen ion concentration alone.

The open circles (o) represent the observed values for powder no. 7, 0-0.2 mm, the lines the prediction of the model.

Figure 7d

The observed dissolution together with the model prediction for a powder well slurried before application.

When the calcite powder is applied dry, a drastic reduction in dissolved fraction can be observed. This is due to agglomeration of the finer particles with the larger ones. The difference may be explained if it is assumed that all particles smaller than 6 microns are absorbed to the larger particles.

(Δ) represents dry application, (o) wet slurried application.

sents the prediction of the model and the observed dissolution for a wet slurried powder. The lower points indicate the observed dissolved fraction when the powder is applied dry. The difference may be explained if it is assumed that all particles less than 6 microns are agglomerated to larger particles. This hypothesis is supported by photographs taken with electron microscope (Sverdrup & Bjerle 1982).

General dissolution diagrams

For a single particle of a mineral sinking in a water column the equation for the dissolution becomes

$$-\frac{dm}{ds} = \beta \cdot \frac{RR}{r_0^3} \quad (46)$$

For a whole powder containing all sorts of particle sizes the expression becomes

$$-\frac{dm}{ds} = \beta \cdot \sum_{i=1}^n \left(\frac{\Delta \phi_i}{r_{0i}^3} \left(RR - \sum_{j=i-1}^{n-1} \frac{m_0 - m_j}{A_L \cdot P \cdot M_E} \right) \right) \quad (47)$$

In the equation (47) is the specific kinetic expression for the dissolution of mineral dissolving. RR is the dissolution rate per unit mineral surface area.

$$RR = (dm/dt) / A_s \quad (48)$$

By inserting RR for a mineral in equation 47, the dissolution may be calculated with the model.

The model has been solved analytically as well as numerically for calcite. A diagram with the expected dissolution for calcite powders with different grinding grade were constructed to aid dose calculation.

Such dissolution efficiency diagrams can be made for all minerals where the kinetical expression RR is known and where the value of the coefficients are known. It is not critical if the backward rate is not known as the backward reaction rate becomes important only at conditions close to saturation. Lake liming is generally carried out in such a way that the conditions in the lake will be far from saturation.

For all the minerals previously mentioned, the rate constants are known. Several were determined by the author, the complete expression for calcite, K1 and KW for dolomite, the complete expression for K-slag and magnesite and K1 and KW for olivine. The rest could be determined from the literature (Plummer et al 1979, Busenberger et al 1982). The numerical values used are listed in table 1.

The computerized model was used to calculate the different dissolution efficiency diagrams for the minerals listed in table 1. Calculations were made for powders with size distribution curves corresponding to nos. 1, 5, 6, 7, 8, 9 and 10. The diagrams are shown in figures 9-12.

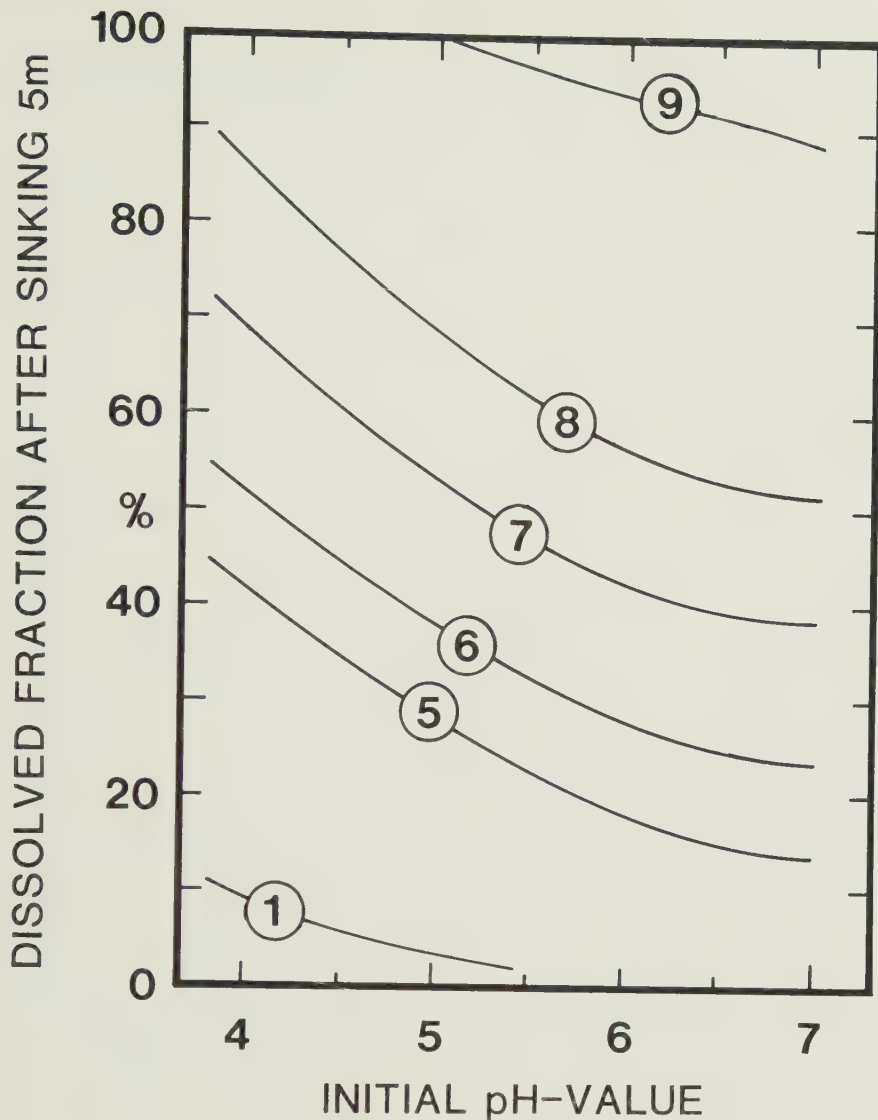


Figure 9

Dissolution curves for calcite; CaCO_3

The dissolved fraction for different calcite powders after sinking through 5 meter of acidic water. The numbers represent particle size distributions as indicated in figure 2a.

Their commercial classification is:

- 1: 0-3 mm Agricultural limestone
- 5: 0-1 mm Agricultural limestone
- 6: 0-0.5 mm calcite powder 0-0.250 mm calcite powder, GG 250
- 7: 0-0.2 mm, 0-0.125 mm, 0-0.1 mm calcite powder, GG 100
- 8: 0-0.05 mm, 0-0.044 mm calcite powder, Mesa
- 9: Chalkfiller
- 10: Marble filler

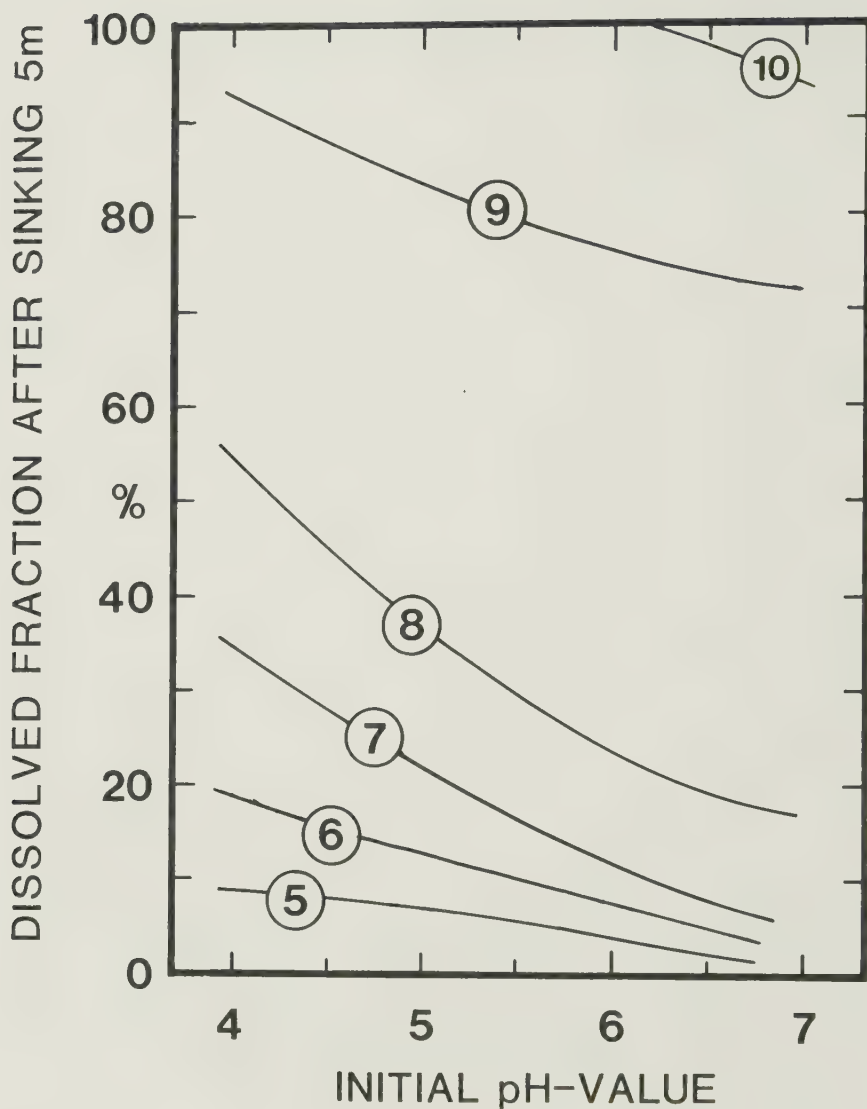


Figure 10

Dissolution curves for Dolomite $\text{CaMg}(\text{CO}_3)_2$.
The dissolved fraction for different dolomite powders
after sinking through 5 meter of acidic water. The
numbers represent particle size distributions as in-
dicated in figure 2a.

For depth other than 5 meter the diagram may be used if
the entering pH-value to the diagram is changed according
to:

$$\text{pH}(\text{diagram}) = \text{pH}(\text{lake}) - 0.5 \cdot \log \left(\frac{\text{actual depth}}{\text{five meter}} \right)$$

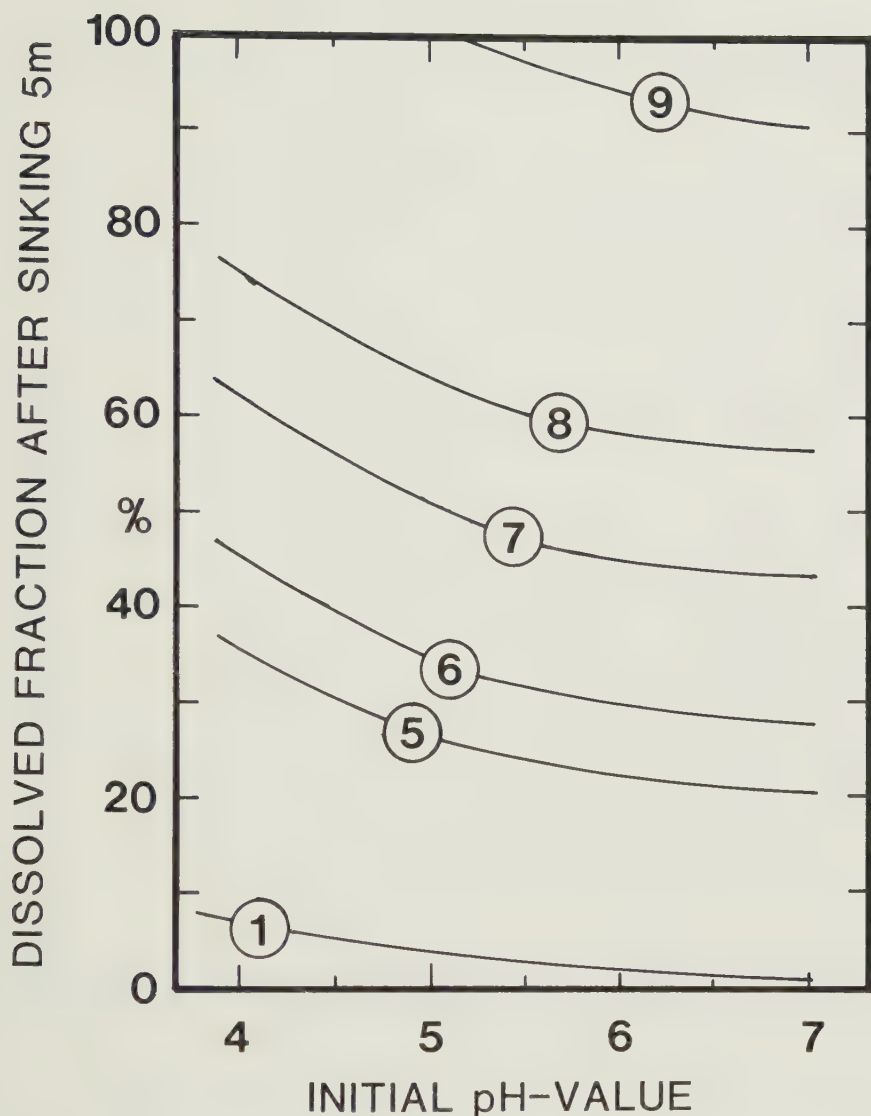


Figure 11

Dissolution curves for K-slag or T-slag; Ca_3SiO_5 . The dissolved fraction for different powders of K-slag after sinking through 5 meter of acidic water. The numbers represent particle size distributions as indicated in figure 2a. K-slag dissolves slightly less than calcite at pH-values below pH 5.5-5.8 and slightly more at higher values.

The diagram may be used for other depths than 5 meter if this is compensated for in the entering value in the diagram according to:

$$\text{pH}(\text{diagram}) = \text{pH}(\text{lake}) - 0.67 \cdot \log \left(\frac{\text{actual depth}}{\text{five meter}} \right)$$

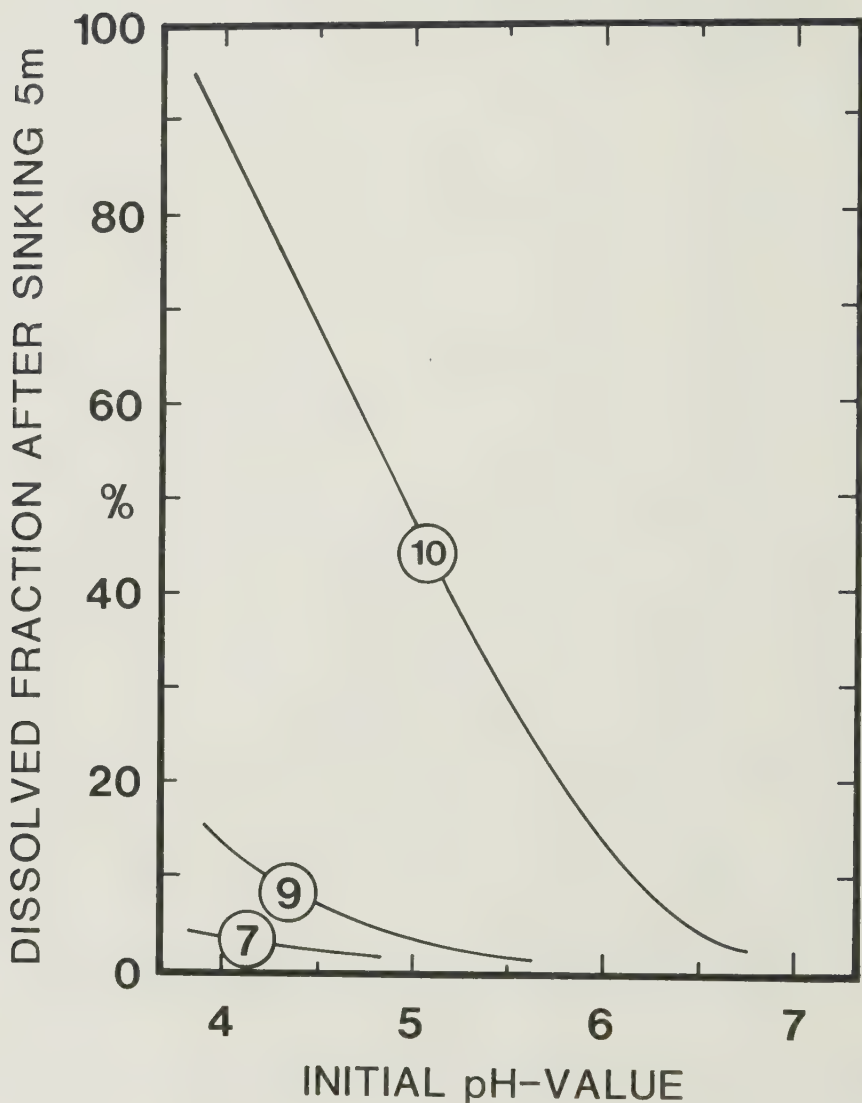


Figure 12

Dissolution curves for olivine; Mg_2SiO_4 .

The dissolved fraction of olivine powders after sinking in 5 meters of acidic water. The numbers indicate the particle size distributions as shown in figure 2a. Only extremely finely ground olivine powders will be able to dissolve to a substantial degree in a normal lake liming.

The diagram may be used for other depths than 5 meter if this is compensated for in the entering value in the diagram according to:

$$\text{pH}(\text{diagram}) = \text{pH}(\text{lake}) - \log \left(\frac{\text{actual depth}}{\text{five meter}} \right)$$

The diagrams show that dolomite must be substantially cheaper than the equivalent grinding grade of calcite or K-slag in order to be a competitive neutralization agent. As dolomite and calcite are usually quarried and processed in the same way, that condition is seldom met.

If olivine is to be used as a neutralizing agent, grinding to an extremely fine powder is required for the mineral to dissolve to a substantial degree. The costs involved in producing such extremely fineground particles are generally such as to exclude olivine as a neutralizing agent for acid lakes.

The effect of magnesite content on the calcite dissolution rate

It is known that contents of magnesite or dolomite in a calcitic limestone will be able to influence the dissolution rate. At higher contents of dolomite or magnesite, the influence may be substantial.

In Sweden, the limestones used for lake liming are generally have a high content of calcite, 90 % CaCO_3 and the rest is usually silica. There are however limestones which contain substantial amounts of dolomite or magnesite, often these are called dolomitic limestones.

In figure 13 a theoretical calculation of the dissolution efficiency for a powder with grinding grade no 7, often classified 0-0.2 mm is shown. The different curves correspond to different proportions of calcite and dolomite in the material. It can be seen that when the content of dolomite exceeds 10-15 % or when measured as MgCO_3 5-8 % or as MgO 3-4 %, the dissolution efficiency declines rapidly.

The curves were calculated using a composite reaction rate RR , defined as

$$RR = X_C * RR_C + X_D * RR_D \quad (49)$$

where X is the fraction calcite in the material, RR_C the reaction rate for calcite, X the fraction dolomite in the material and RR_D the reaction rate for dolomite.

The effect of temperature on the dissolution in lakes

The effect of the temperature on the dissolution of neutralizing agents have often been raised. Plummer et al (1979) and Busenberger et al (1982) determined the temperature dependency of the rate constants for calcite and dolomite.

The dissolution of calcite is for temperature below 25°C a completely diffusion controlled process. Accordingly its rate of dissolution is rather insensitive to temperature variations. The activity of the hydrogen ion will increase with increased temperature, causing the dissolution to proceed faster. But the kinematic viscosity will decrease at the same time and cause the particles to sink faster to the bottom. The two factors very nearly cancel each other out.

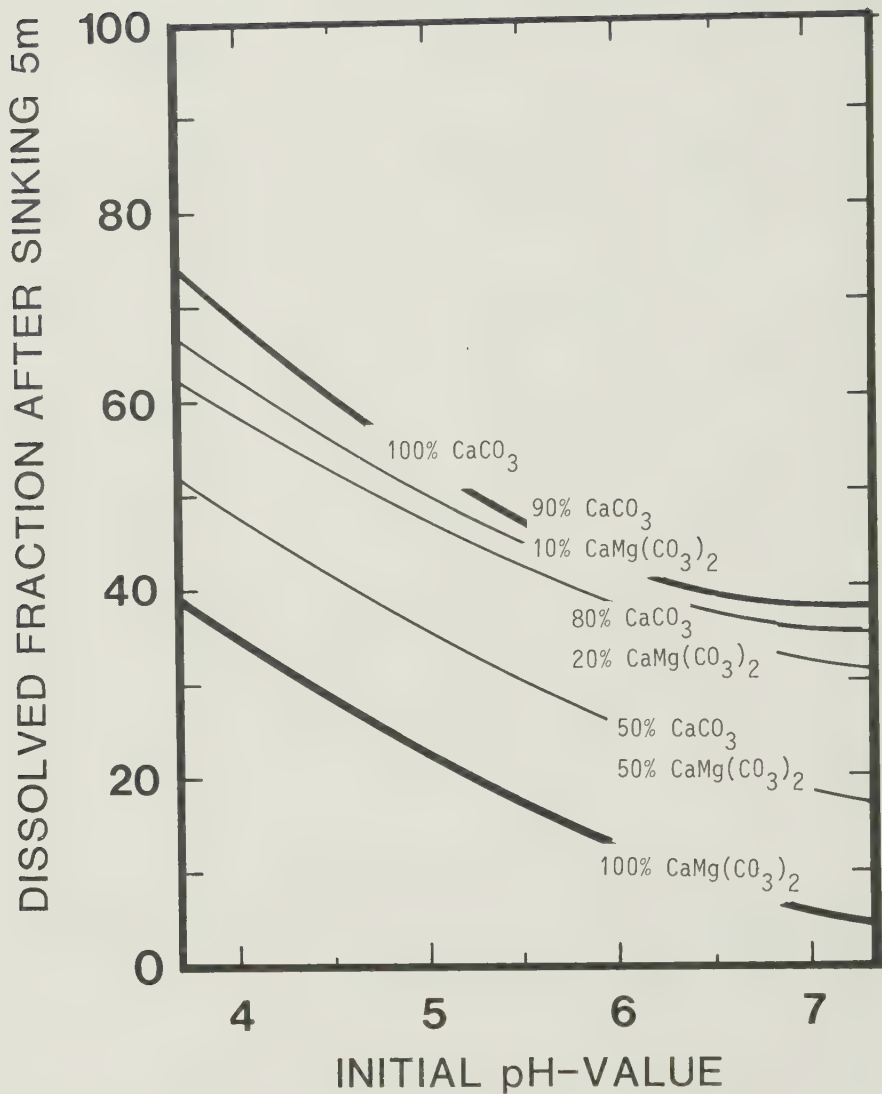


Figure 13

The dolomite content of a natural calcite will be able to influence the fraction dissolved in a lake liming. The diagram shows the dissolution curves for powder no. 7, called 0-0.2 mm, with increasing contents of dolomite.

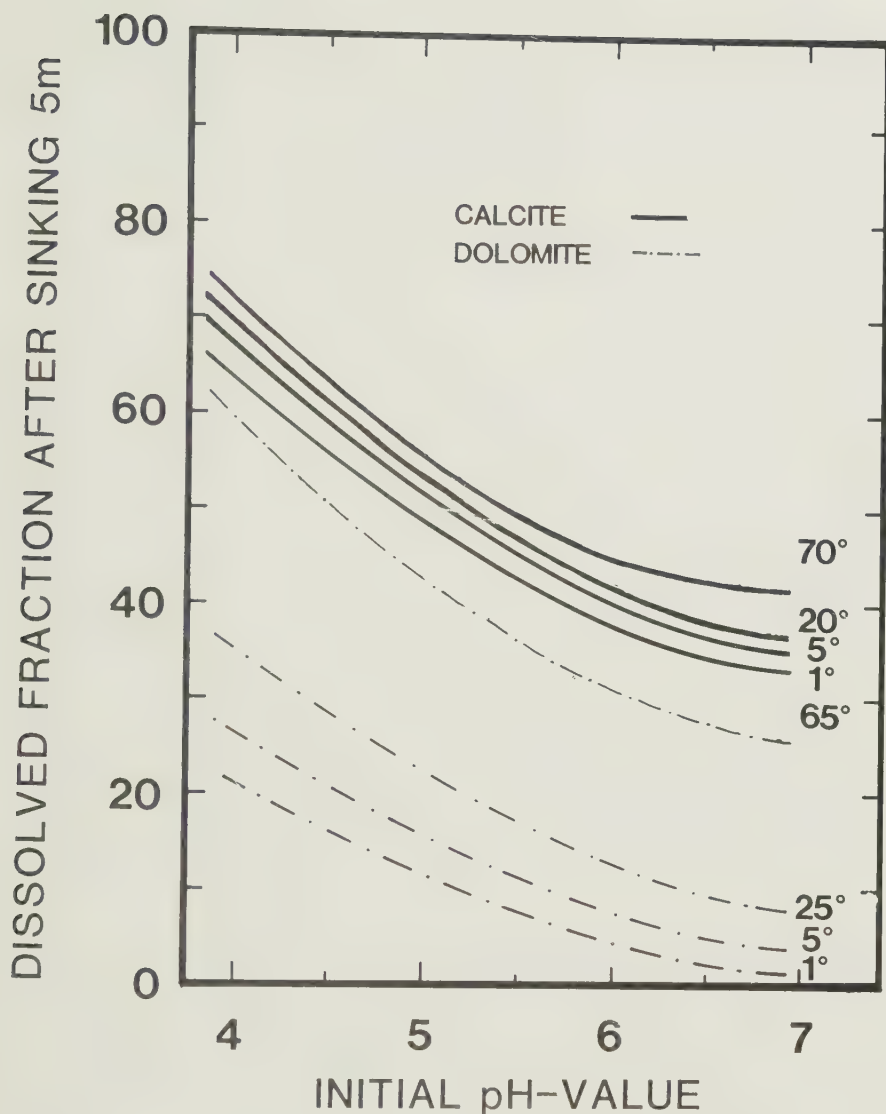


Figure 14

The dissolution of calcite is a diffusion controlled process and as such not very sensitive to temperature changes. The activity of the hydrogen ion will increase with the temperature, causing the dissolution to proceed faster. But at higher temperatures the kinematic viscosity decreases causing the particles to sink faster. The two factors very nearly cancel each other out. The dissolution of dolomite is however kinetically controlled, and rather sensitive to temperature changes. At temperatures above 65°C the dissolution of dolomite becomes diffusion controlled and as rapid as the dissolution of calcite. The curves shown apply to a calcite powder with sieve curve no. 7, commercially called 0-0.2 mm.

For dolomite the situation is different. The dissolution rate for dolomite is kinetically controlled by the chemical reaction on the surface and accordingly sensitive to temperature variations. At higher temperatures the chemical reaction of dolomite with the hydrogen ion becomes so rapid that the process becomes diffusion limited and first order with respect to the hydrogen ion. The transition takes place at approximately 65-70°C. At temperatures above 85°C, dolomite will dissolve as fast as calcite.

The dissolution curves for powder no. 7, called 0-0.2 mm, at different temperatures are shown in figure 14.

Important parameters

There are several parameters influencing the dissolution efficiency and neutralization achieved observed in lake liming. The dissolution model identifies the strongest acting parameters in order of importance

- Calcite powder grinding grade
- Initial pH-value of the water
- Sinking depth
- Degree of wet slurring prior to application

for dosages in excess of 25 g/m^3 the dose will be of major importance

The dose per unit volume

A magnesium carbonate content in excess of 5 % may reduce the dissolution rate for the mineral significantly

Magnesium carbonate content

Other significant parameters, but of less importance, are:

- Slope of the titration curve
- Vertical convection and mixing in the lake
- Temperature of the water column

Certain parameters are of little significance:

- Carbondioxide content of the water
- Geological origin of the calcite

Several of the listed parameters are given as soon as a lake has been chosen for liming. The design parameters are those that may be manipulated regardless of the conditions on the location. In Sweden generally high calcium calcites are considered, and the dominating design variabel will therefor be the grinding grade.

A case study, 4 Swedish lake limings

A Federally-funded National Swedish Liming Project was initiated in early 1977 as a five-year pilot program. During this period, the government initiated 450 liming projects resulting in the treatment of more than 1500 water bodies. Unfortunately the projects were more operational than experimental. The scientific basis for the program was rather weak, therefore only a limited amount of reliable information can be obtained from the data collected from those studies.

In earlier work we relied upon data from a large number of lake limings carried out in the years 1974-1981 and the data may be found in the official files at the Swedish Board of Fisheries at Göteborg (Sverdrup 1983). Closer studies of these data have indicated that the accuracy of the data in these files and accordingly the information used by us is much less precise than earlier assumed.

The actual projects often included mixed efforts such as deep water liming, application in the littoral zone and on the beaches as well as liming of adjoining soils. In relation to the model the definition of a relevant sinking depth for liming in the littoral zone becomes very difficult. The files do not generally contain any information on the degree of wet slurring of the powder prior to application. Five to ten years after the actual application such information has been difficult to obtain from the entrepreneur carried out the actual calcite addition.

The calcite powders used for liming are generally reported by their commercial name and particle size distribution curves are generally missing. Later studies (Sverdrup et al 1985) have shown that manufacturers of calcite powders would often market powders with different particle size distribution curves under the same commercial name. The datasets used earlier are accordingly not as relevant for testing the model as assumed. A small number of the datasets permits qualitative analysis and a limited number allows quantitative analysis (Sverdrup & Warfvinge 1984).

Here we will present new information on which the model may be tested, data of a quality superior to what has been available earlier.

In the spring of 1985 several lakes were limed in a project designed to test the dissolution model. In the project the lakes were monitored for a year before liming and after liming with depth profiles at frequent intervals. All parameters related to the dissolution of calcite was closely monitored in order to rule out uncertainties experienced in earlier studies.

Lake Mäsen was limed over the whole lake surface area from a boat distributing a powder with a grinding grade equivalent to sieve curve no. 7. The powder was applied after wet slurring. The lake is large and deep, the volume is 96 million cubicmeter, the average depth 23 meter. Prior to liming the lake had a pH-value of pH 5.7.

*** Dissolution of calcite powder sinking in acid water ***

Lake name	Mäsen
Calcite powder	0-0.2 mm/No.7
Initial pH-value in the lake	pH 5.7
Lake depth on the location of appl	15 meter
Dose for the whole lake volume	17.3 g / m ³
Fraction of the lake surface treated	80 %
Calciumcarbonate content of calcite	85 %
Slope of the titration curve	7.2 g CaCO ₃ /m ³ ·pH

Mean diameter micron r_i	Size fraction ϕ_i	Dissolved fraction X_i
140	0.02	0.0008
96	0.11	0.0025
56	0.10	0.0125
39	0.14	0.0373
28	0.08	0.0976
20	0.10	0.2450
14	0.05	0.5580
10	0.06	0.8994
6	0.14	1.0
3	0.09	1.0
2	0.08	1.0
1	0.06	1.0

Total fraction dissolved	47.1 %
The calcium concentration will increase	2.77 g/m ³
The pH-value will after mixing become pH	6.65

Table 3 Model printout for the liming of lake Mäsen.
Actual values from the liming is used as indata

The translated printout of a run with the model is shown in table 3, predicting the dissolution of the added calcite in the water column.

Three lakes in the project were limed with airdrops of dry powder. For powder applied dry we have assumed that particles less than 6 microns were agglomerated with coarser particles. The observed dissolution efficiencies seem to support this assumption. The observations are summarized in the tables 4 a and 4 b.

Two lakes in Bohuslän on the Swedish West Coast, Sandvatten and Husebotjärn were limed with dry airdrops of a powder equivalent to no 7 (0-0.2 mm). Sandvatten is a deep lake for its size. In the province of Halland, lake Furesjön was limed with dry airdrops of a powder equal to powder no. 5.

In the summary in table 4 a we have assumed that particles less than 6 microns were agglomerated with coarser particles. The observed dissolution efficiencies seem to support this assumption.

Case study: Sandy lake, Nova Scotia, Canada

The lake liming of Sandy lake, was described by W.J. White, Walton Watt and G.D. Scott (1984). The lake was limed in such a way that the case may be used to test the dissolution model.

In the article the authors define the particle size distribution of the calcite powder used as having 85 % of the particles less than 100 microns and 15 % less than 10 microns and an average diameter of 35 microns. This information makes it possible to draw an approximate line in the size distribution diagram (figure 15).

The powder was well stirred and mixed in a tank before distribution on the lake, according to the authors. The calcite was spread evenly over the lake surface from a boat. The lake was limed with 135 tons of calcite, the calcium carbonate content was 88 %.

Sandy lake is a clearwater lake, it has a volume of 5.1 million cubic meter and an average depth of 6.9 meter.

The authors present an integrated mass balance for calcite in the article which gives information on the observed instant dissolution of calcite, as well as the long term dissolution.

On the diagram in figure 16 we have drawn the theoretical dissolution line for the calcite powder used and entered the observed value as a circle.

The conditions in the lake prior to liming may be entered in the diagram at the indicated line. The necessary indata for reading the diagram is:

Initial pH-value in the lake	pH 4.9-5
Average sinking depth for the calcite	6.9 meter
Entering point in the diagram	pH 4.8-4.9

Lake	Powder no	Application mode	Initial lake pH	Sinking depth (m)	Total amount (ton)	CaCO content (%)	Observed dissolution (%)	Pred. wet slurried diss. (%)	Pred. dry app diss. (%)
Mäsen	7	Wet slurried	5.7	15	1700	85	42-45	47.1	-
Sandvatten, Bohuslän	7	Dry airdrop	4.7	10	65	85	34-36	56.1	33
Husebotjärn, Bohuslän	7	Dry airdrop	5.4	5	20	85	33-35	42.5	30
Furesjön, Halland	5	Dry airdrop	5.9	5	65	90	23-27	24.5	22

Table 4 a Data from the project "Sjökalkningen med kalkstensmjöl av olika malningsgrad" may be used to test the dissolution model for dry drop and wet slurried application as well. The computerized model was used to predict the wet slurried dissolution

Lake	Observed final lake pH-value	Model prediction and target value	Deviation absolute	Deviation % of pH-elevation observed
Mäsen	6.85	7.0	-0.15	-13,6
Sandvatten	6.1	6.1-6.3	+0.10	+ 7.1
Husebotjärn	6.5	6.5-6.6	+0.05	+ 9.5
Furesjön	6.85	7.0	+0.15	+16.6

Table 4 b The table show the observed results in comparison with the mode prediction based on the conditions in the lakes just before liming

The calcite dose was 26.7 g/m^3 and the size of the dose ought not to influence the dissolution rate significantly.

We can read the predicted dissolution rate:

Predicted instant dissolution	33-35 %
Observed instant dissolution	35-36 %

A further evaluation of dose-chemical response is not possible without access to the tabulated values. As the concentrations of calcium and pH are only given as diagrams.

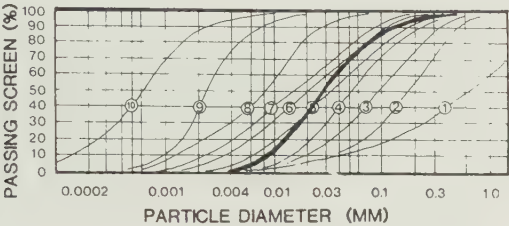


Figure 15 The particle size distribution of the calcite powder used for the liming of Sandy Lake as reported by White et al (1984).

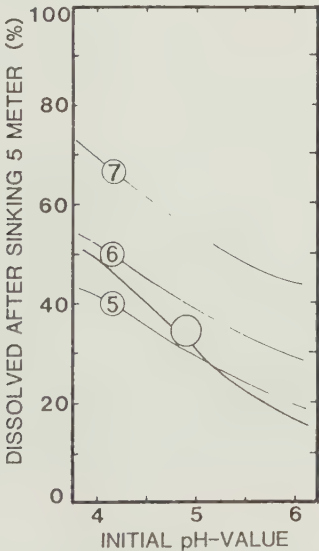
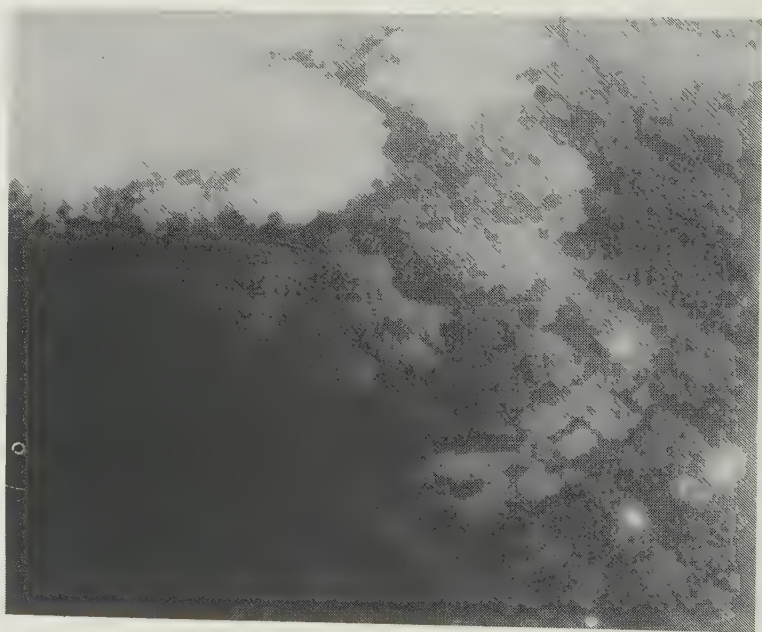
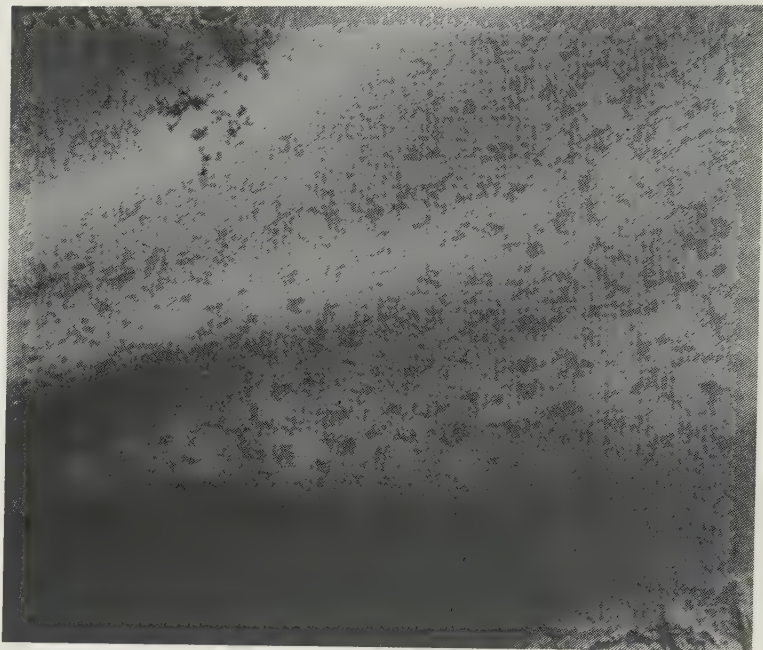


Figure 16 The dissolution line for the powder used to lime Sandy Lake, Nova Scotia, was calculated and entered in the diagram. The circle represents the observed value as reported by White et al (1984). The powder was applied as a well stirred slurry over a large fraction of the lake surface area.



The application of the calcite powder evenly over the whole lake surface ensures a good dispersion of it in the water column. When large amounts are spread in a small area, as in littoral zones, or by applying a wet slurry with high solid material content, plumes of higher density may form that will sink faster to the bottom. The photographs were taken during the liming of Stora Le, a lake which is 120 km long. It was limed with 9000 tons of calcite.

3. REACIDIFICATION OF LIMED LAKES

Introduction

When lakes are neutralized with calcite powder, the amount added is intended to neutralize the water column as well as to delay reacidification as much as possible. The reacidification of a limed lake is dependent on the dilution of the dissolved calcium carbonate with time and for a limited period of time after liming, dissolution of residual calcite from the bottom as well as ion exchange with the sediments.

Calcite in the sediments will be able to create such conditions that precipitation of iron complexes and humates form on the mineral surfaces. This process will be able to deactivate most of the available calcite surfaces in 1-2 years, reducing the dissolution rate substantially.

Model concept

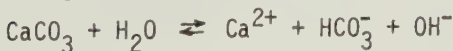
A model was developed, in order to calculate the reacidification of a limed lake. The following mechanisms were assumed to participate in the reacidification process:

- The dissolution of calcite and a subsequent neutralization of acid water.
- Due to the increase in pH-value close to the calcite mineral surface, precipitation of complexes of iron and humates on the mineral surfaces will occur, hindering dissolution.
- Sediments with no calcite cover reversibly sorb calcium from the water column.
- All transport of mass between the sediments and the water column is assumed to take place by diffusion.

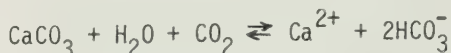
As a first approach the lake was modelled as a stirred tank. The equations were formed as a mass balance for dissolved calcite, including the dissolution kinetics for the mineral, in order to describe the long term development of pH, alkalinity and calcium concentration of the lakewater.

The chemical model

When calcite dissolves in sediments, two reactions will be of major importance:



The reaction with carbondioxide is of less importance:



The reaction with carbondioxide does not contribute significantly to the overall dissolution rate at carbondioxide pressures below 0.1 atm in stirred solutions.

In lakes the carbondioxide pressure seldom exceeds 0.005 atm in the water column, but concentrations as high as 0.02 atm have been observed in the water just above the sediments (Hindar & Nilssen 1984). Typical are variations in the range 0.005-0.01 atm. Deeper in the sediments the partial pressure could probably be as high as 0.1 atm.

During the stagnation period the increased thickness of the boundary layer could alter the boundary conditions, increasing the contribution of the reaction with carbondioxide to the overall rate. In the model this contribution was considered to be small and rather constant and it was incorporated into the water reaction constant, KW.

$$\text{RR} = K_1 \cdot [\text{H}^+] + \text{KW} - \text{KB} \cdot [\text{Ca}^{2+}] \cdot [\text{HCO}_3^-] \quad (50)$$

where K_1 was set at $1.5 \cdot 10^{-7}$ m/s corresponding to a boundary layer thickness of approximately 6 microns. The reaction of calcite with water is no longer limited by the kinetic rate but the rate of diffusion of the products into the water column. In the model KW was set at $1.4 \cdot 10^{-11}$ kmol/m²·s, assuming

$$\text{KW} = \text{KW}(\text{H}_2\text{O}) + \text{KW}(\text{CO}_2) \quad (51)$$

where $\text{KW}(\text{H}_2\text{O}) = 8 \cdot 10^{-12}$ kmol/m²·s and $\text{KW}(\text{CO}_2)$ will be given by the diffusion of CO₂ to the mineral surface through the boundary layer:

$$\text{KW} = 1.2 \cdot 10^{-9} \cdot P(\text{CO}_2) \text{ kmol/m}^2 \cdot \text{s}$$

The significance of the carbondioxide partial pressure may be illustrated as follows of table 5.

P_{CO_2}	$\text{KW}(\text{CO}_2)$	KW
0.020 atm	$2.4 \cdot 10^{-11}$	$3.2 \cdot 10^{-11} \text{ kmol/m}^2 \cdot \text{s}$
0.010 atm	$1.2 \cdot 10^{-11}$	$2.0 \cdot 10^{-11} \text{ kmol/m}^2 \cdot \text{s}$
0.005 atm	$0.6 \cdot 10^{-11}$	$1.4 \cdot 10^{-11} \text{ kmol/m}^2 \cdot \text{s}$
0.002 atm	$0.3 \cdot 10^{-11}$	$1.1 \cdot 10^{-11} \text{ kmol/m}^2 \cdot \text{s}$

Table 5 The influence of the carbondioxide pressure on the reaction rate when incorporated into the water reaction rate constant

KB was set to the value $4 \cdot 10^{-9} \text{ m}^4/\text{kmo1} \cdot \text{s}$.

The model was run in two versions, one with the full expression for the dissolution rate as in eq (40) and one version with a truncated version of the rate expression

$$\text{RR} = K_1 \cdot [\text{H}^+] \quad (52)$$

The expression for the dissolution rate becomes

$$-\frac{dm}{dt} = \text{RR} \cdot A_s \cdot \psi(t) \quad (53)$$

where RR is the dissolution reaction rate, A_s the area of mineral surface exposed to the water and $\psi(t)$ the deactivation function. The deactivation function is derived from the mechanisms of surface deactivation (Levenspiel 1975) and given by

$$\psi(t) = e^{-KH \cdot t + KH_0} \quad (54)$$

KH usually has a value in the range $0.5\text{--}1.0 \text{ yr}^{-1}$ and KH_0 is equal to $10^{-5}\text{--}10^{-6}$. The value for KH_0 implies that deactivation does not completely stop the dissolution but may bring it down to a very low level.

The hydrology of very large chemical lake reactors

The flushing rate and the degree of mixing in most lakes vary substantially with the seasons, due to seasonal tributary flow rate variations and the thermal stratification of lakes.

In shallow lakes the thermocline may reach such a depth that the volume of the hypolimnion becomes small compared to the total lake volume. In such a case the stratification of the lake will have little influence on residence time variations in relation to the variations induced by flow rate fluctuations. Accordingly shallow lakes may be modelled as one stirred tank with variable flow rate.

The residence time variations will be influenced both by the stratification and the flow rate variations if the lake is deep and/or has a short mean retention time. A two tank model is needed to model such a system adequately.

In deep lakes where the mean residence time is considerably longer than each stratification period, the lake may be considered as fairly well mixed during one residence time period. Such a lake may well be modelled by one stirred tank model.

Two different model structures of different complexity were devised, in order to be able to handle all kinds of lakes. The first and simplest structure for a lake system is shown in figure 17 a. Each lake in a river system is modelled as a stirred tank reactor with variable flow and dissolution of calcite on the bottom.

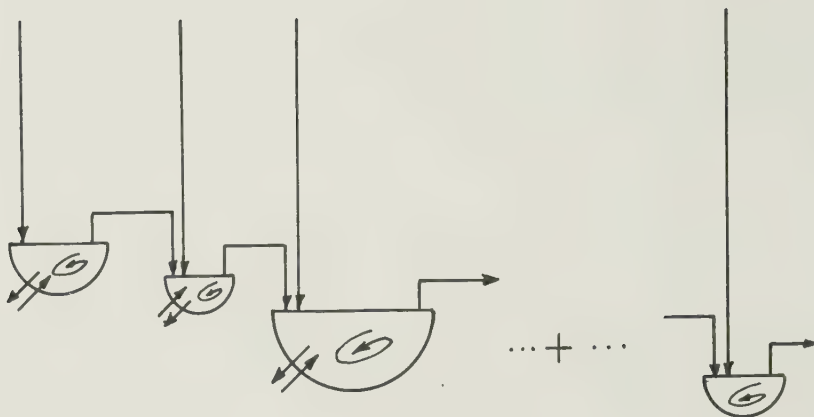


Figure 17a

The reacidification model, pictures every lake as a stirred tank with variable flowrate. The model works well in lakes where the volume of the hypolimnion is small compared to the total volume or in lakes where the retention time is longer than 1.5 years.

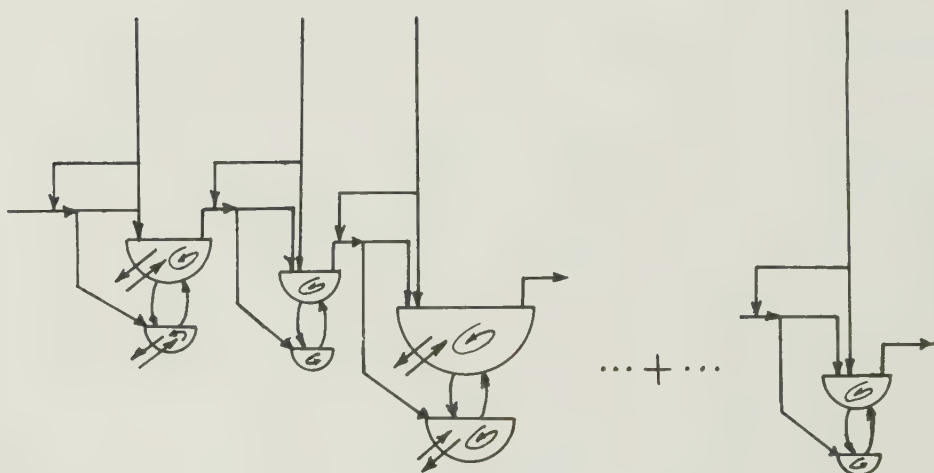


Figure 17b

A more complicated model structure was tried in order to account for short term changes such as thermal stratification. The model is successful in modelling such changes but generally requires more data than what is available in Swedens operational lake liming program.

The more complex structure is shown in figure 17 b. It consists of two tanks for every lake to account for the effect of stratification. At every turnover in the fall and the spring the two tanks are merged.

The complex model requires more input data for the initial chemical condition as well as physical data needed for the calculation of the position of the thermocline.

However, most lakes in Sweden will fall into the categories defined earlier that may be modelled with single tank models, the more complex model was abandoned after completion, to the benefit of the simpler concept. A contributing factor for this was that the input data required by the complex model is not generally available for Swedish lake liming projects, whereas the data available will suffice for the simpler concept.

The mass balance equations used

For each tank in the model structure a mass balance for calcium and hydrogen ion in the water column is made, for the hydrogen ion:

tributary input = accumulation + neutralized + outlet transport

For calcium:

tributary input + dissolved = accumulated + outlet transport

From the input data an equilibrium curve is calculated which is used to determine the alkalinity and pH after equilibration of the dissolved amount.

The mass balance equation becomes, for the hydrogen ion:

$$\frac{d[H^+]}{dt} + (1/T)[H^+] + (P/S)(e^{-KH \cdot t} + KH_0) \cdot RR = (1/T) \cdot [H^+]_{in} \quad (55)$$

where P is the ratio between the available mineral surface area on the bottom and the bottom surface area itself. T is the residence time for the lake and it is variable with time, depending on the flowrate Q and the lake volume V

$$1/T = Q(t)/V \quad (56)$$

In the model the lake volume is kept constant but the flowrate will vary with the seasons, making variable with time.

The mass balance for calcium becomes:(57)

$$\frac{d[Ca^{2+}]}{dt} + (1/T) \cdot [Ca^{2+}] = (P/S)(e^{-KH \cdot t} + KH_0) RR + (1/T) \cdot [Ca^{2+}]_{in}$$

For constant , an approximation applicable to lakes with very long retention times, the differential equations may be solved analytically. The analytical solution is of more theoretical interest and its practical application limited.

Numerical calculations are much more useful for practical purposes and the reacidification for any lake may be modelled with the aid of a small computer.

Model development

The model was tried on a large number of lakes as well as lakes in series. However, in its initial version, the model predicted the general trend of reacidification, but not the short time seasonal variations. Such a calculation is shown for lake Övre Bolsjön in figure 18.

The calcium concentration and the mass balance for dissolved calcite are predicted, but the alkalinity and the pH-value fluctuate more than predicted by the model.

The temperature of the water column varies substantially over the year. In the epilimnion it may fluctuate between +0°C in the winter and +20°C in the summer. In the hypolimnion the fluctuations are less, from +4°C to approximately 10-12°C at maximum.

The dissolution processes are limited by diffusion in a lake and therefore not very sensitive to temperature variations of the indicated magnitude. But the chemical equilibrium between dissolved calcium carbonate and alkalinity and pH-value will be influenced by the temperature. The induced change in pH and alkalinity will in addition be amplified by withdrawal of carbondioxide by biological activities in the upper part of the epilimnion. The performance of the model improved when the mentioned factors were considered in the calculation of alkalinity and pH.

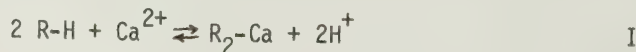
A recalculation with the improved model for the reacidification of lake Övre Bolsjön is shown in figure 18. The revised model predicts the short term fluctuations as well as the general reacidification trend.

Another perhaps more reasonable approach would be to model the mass balance based on alkalinity. If the mass balance for the hydrogen ion is viewed as a balance for the acidity however, that might be an equivalent concept.

It is interesting to note that the model works well even when the reaction of calcite with the hydrogen ion only is considered.

Ion exchange with lake sediments

Several stoichiometries may be deduced for the ion exchange of calcium and hydrogen ions in the water column with the sediments. We may assume the ion exchange site to change from monovalent to divalent:



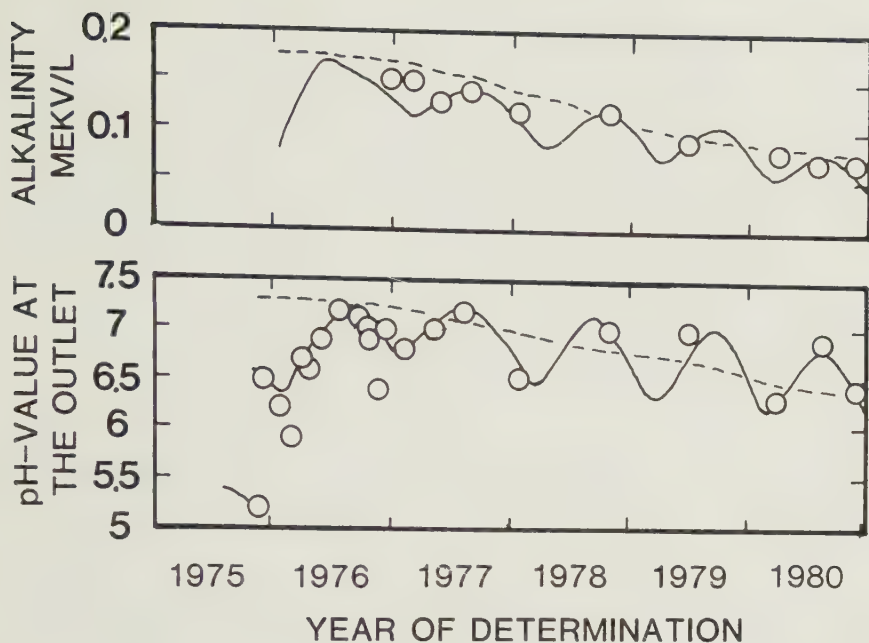


Figure 18

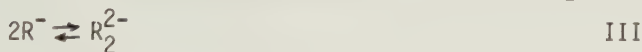
In its first version the reacidification model was not very dynamic. The dotted line represents the first published calculation for the reacidification of lake Övre Bolsjön in the Province of Bohuslän. The lake has a retention time of 3.6 years and a volume of approximately 17 million m^3 , and was limed with 500 tons of calcite (Sverdrup et al 1984).

The drawn line (—) represents the recalculation with the improved model which predicts the observed short term variations well. The circles represent the observed values from the lake outlet.

or divalent:



In the first mechanism the change from R^- to R_2^{2-} is implicated:



The two stoichiometries result in different rate expressions and different selectivity coefficients (Sverdrup & Warfvinge 1985, Warfvinge & Sverdrup 1985).

For the first reaction alternative we get the selectivity coefficient:

$$K_I = \frac{[R-H]^2 \cdot [Ca^{2+}]}{[R_2-Ca^{2+}] \cdot [H^+]^2} \quad (58)$$

or for the second ion exchange reaction (II):

$$K_{II} = \frac{[R-H_2][Ca^{2+}]}{[R-Ca^{2+}][H^+]^2} \quad (59)$$

Ion exchange studies have left the impression that the exchanger phase is a multivalent matrix, not very specific with respect to valence. For such an ion exchange substrate the second expression may be more appropriate (Sverdrup & Warfvinge 1985, Warfvinge & Sverdrup 1985).

The dissolution of calcite of a lake bottom is diffusion controlled and it is highly probable that the ion exchange between the water column and the sediments are diffusion controlled as well.

The forward step, calcium ions entering the sediment will be dependent on the calcium diffusion into the sediments. The diffusion will be dependent on the gradient into the sediment. If we assume pseudo-steady state in the boundary layer we may write:

$$\frac{\partial SA}{\partial t} = (KA \cdot ([Ca^{2+}] - [Ca^{2+}]_s) \cdot (1-P) \cdot A_L \quad (60)$$

where A_L is the lake bottom area, $(1-P)$ the fraction of the bottom area not receiving calcite. KA is the mass transfer coefficient for calcium and assuming the boundary layer to be as stated earlier, 6-10 cm thick, KA will have a value in the range 0.3-0.6 m/yr.

The calcium concentration in the sediment is given by the equilibrium with the ion exchange material:

$$[Ca^{2+}]_s = \frac{SA/SM}{1 - SA/SM} \cdot K_{II} \cdot [H^+]^2 \quad (61)$$

where K_{II} is the selectivity coefficient and (SA/SM) the base saturation of the sediments. SA is the amount absorbed to the sediments:

$$SA = R-Ca$$

$$SM = R-Ca + R-H_2$$

The expression for the reversible sorption of calcium to the sediments then becomes:

$$\frac{dSA}{dt} = KA \cdot ([Ca^{2+}] - \frac{SA/SM}{1 - SA/SM} \cdot K_{II} \cdot [H^+]^2) \cdot (1 - P) \cdot A_L \quad (62)$$

The reacidification model is capable of predicting the reacidification with good accuracy, without the incorporation of a sediment module in the model.

The incorporation of the sediment ion exchange module in the model is probably as far as it is reasonable to go with such a simple one tank model. It represents such a degree of refinement that further development would have to consider the stratification of lakes as well. A two tank model would then be more appropriate.

The academic value of such a model is considerable and it is a valuable and necessary tool for investigation of watercolumn sediment interactions.

A sensitivity analysis of the reacidification process

With the reacidification model we may carry out a sensitivity analysis of the parameters controlling the reacidification rate for a limed lake. By varying them one by one while the others are kept constant we can study their importance.

The most important factors for the reacidification rate may be identified to be:

- the hydraulic residence time
- the acidity of the tributaries
- the amount calcite on the bottom
- the fraction of the bottom with calcite cover

Other important factors are:

- sediment-lake water interaction
- calcite deactivation
- supply of organic material from the tributaries

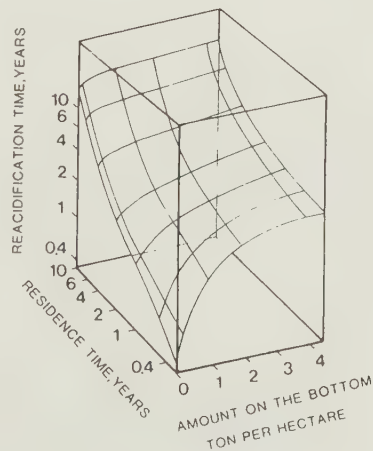
The parameters last mentioned have a significant influence on the reacidification rate, but are less important compared to the first four mentioned, or do not vary significantly between different lakes. Accordingly they may be approximated as constant.

Wave action in the littoral zone has only marginal effects, its importance for the reacidification rate has been much overestimated in earlier assumptions (Bengtsson et al 1980, Wright 1984). Biological activity tends to amplify the seasonal variations but the long term net effect on the reacidification rate is small.

In figure 19 the response-surface for the reacidification time to pH 6 is shown in terms of the residence time och the amount calcite on the bottom, expressed as ton/hectare.

Figure 19

Response surface for the time required to reacidify a lake as a function of the residence in years and as a function of the calcite amount on the lake bottom. It may be seen that doses in excess of 2-3 tons per hectar have little significant effect on the time required for reacidification. As soon as the dose on the bottom exceeds 0.3 ton/Ha, additional amounts of calcite on the lake bottom will not be able to produce proportionally equal increase in the time required to reacidify the lake.



It may be seen from the figure how the reacidification time levels off as the amount on the bottom increases. Thus the benefit of adding excessive amounts of calcite is limited.

There is certain limits to what amounts of calcite that will be able to dissolve of a lake bottom. These amounts which are dependent on the hydraulic retention time, are however greatly in excess of the economical optimal amounts.

Lake retention time	Maximum amount dissolved of the bottom	Economical optimum
More than 5 years	0.5-1 ton/ha	0.3 ton/ha
5-2 years	1.5-1 ton/ha	0.4 ton/ha
2-1 years	1.5-2 ton/ha	0.5 ton/ha
less than 1 year	2-3.5 ton/ha	0.5 ton/ha

Table 6 Only a certain amount of calcite will be able to dissolve off a lake bottom due to deactivation of the mineral surfaces and sedimentation of detritus. The economically optimal dose is however substantially smaller

Amounts in excess of the indicated values will under normal conditions not dissolve within reasonable time limits and the rate of dissolution to slow to be able to delay reacidification of the lake further. The amounts indicated is applied to a situation where the lake is allowed to reacidify to pH 5.4-4.8. The amounts may be substantially smaller in a situation with reliming of the lake at pH 6.2-6.0

The reacidification diagram

With the model, we may make a large number of readicification calculations. From these we can make a diagram, as shown in figure 20.

In the diagram we have plotted the time required to reacidify a limed lake to pH 6 versus the residence time for the lake and the sediment calcite load factor B. This factor takes the effect of the amount calcite on the bottom, the fraction of the bottom with calcite cover and accordingly the sediment-lake interaction into account. It is defined as:

$$B = \left(\frac{MB}{AL} \right) * \left(\frac{P}{0.20} \right) \quad \text{ton/hectare} \quad (63)$$

MB is the residual amount calcite on the bottom after liming, AL the lake surface area, and P the fraction of the bottom with calcite cover. The diagram applies to a situation where the tributaries have their lowest annual pH-value around pH 4.4-5.0.

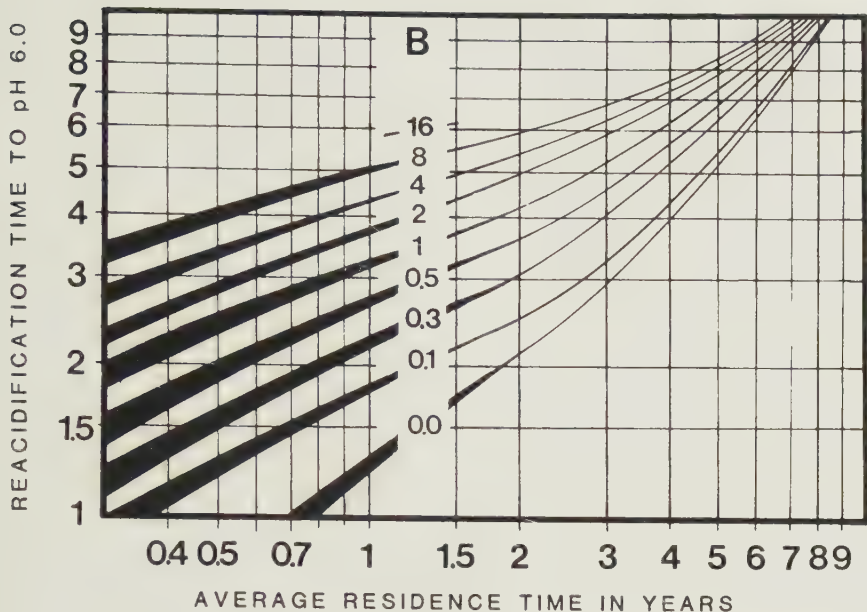


Figure 20

The reacidification nomograph. The time required to reacidify a limed lake to pH 6.0 may be read from the diagram when the residence time of the lake is known. The factor B is the bottom calcite load factor, defined as:

$$B = \left(\frac{\text{Amount calcite on the bottom}}{\text{Lake surface area}} \right) * \left(\frac{P}{0.20} \right) \text{ (ton/ha)}$$

The nomograph is calculated using the assumption that the lake has been limed to a pH level in the range pH 6.5-7.5 and an alkalinity of 0.1-15 mekv/l. The acidity of the tributaries were assumed to be in the range pH 4.8-5.4

P may often be estimated from the detail plan for the actual application of calcite on the lake. Due to limitations in the physical capabilities of lake liming methods, P does seldom exceed 0.50. A typical value for P would be 0.15-0.20. When great emphasis is put on liming in the littoral zones only, P is usually less than 0.10.

The calcite powder will hardly be distributed over more than 50-60 percent of the lake surface, except for very small lakes (even when the application is carried out in the best of ways), due to physical limitations in the application methods used today.

The reacidification rate varies significantly with the seasons, and the big leaps usually occur during the hydrological events in the spring or in the fall. This must be taken into consideration when the diagram is used.

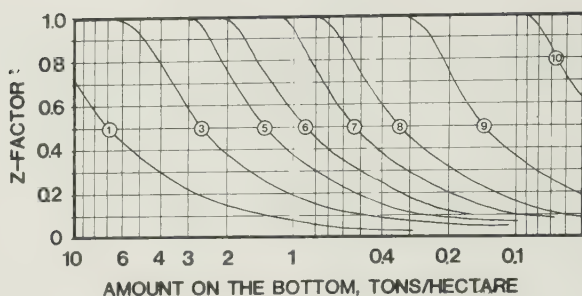


Figure 21 The P factor is estimated from the calcite application plan as the fraction of the lake surface covered by calcite. For lower dosages the powder will not be able to cover the ground upon which it rests completely and P must be reduced with the factor Z, given in this diagram.

When liming with small dosages or coarser powder, the calcite powder may not be able to cover the surface upon which it is resting. Then P must be adjusted for this by a factor Z which may be found in the diagram in figure 21. P will then be:

$$P(\text{ACTUAL}) = P * Z \quad (64)$$

If P cannot be estimated as indicated assume as in table 7:

Method of application	Lake size	P-value
Lake liming by boat over the whole lake surface area, powder wet slurred	I Small lakes, less than 20 ha	P = 0.5-0.8
	II Medium size lakes 200-200 ha	P = 0.2-0.5
	III Large lakes, more than 200 ha	P = 0.10-0.25
Aircraft application over the whole lake surface area	I Small lakes, less than 20 ha	P = 0.25-0.5
	II Medium size lakes 20-200 ha	P = 0.10-0.30
	III Large lakes, more than 200 ha	P = 0.05-0.20
Lake liming by boat over the littoral zones only	I Small and middle size lakes, less than 200 ha	P = 0.03-0.10
	II Large lakes, larger than 200 ha	P = 0.01-0.05
Lake liming by truck over the whole lake surface on the winter ice	I Small and medium size lakes, less than 200 ha	P = 0.05-0.20
	II Large lakes, larger than 200 ha	P = 0.01-0.15

Table 7 Estimates of the value of the P-factor for different lake liming situations

Of the total amount calcite added to a lake, one part will dissolve during sinking, and the rest will settle on the bottom, this amount we will call MB. If the dissolution efficiency is known; X, MB is easy to calculate from the total amount added, TM:

$$MB = (1-X) * TM \quad (\text{tons}) \quad (65)$$

The dissolution efficiency, X, is easy to estimate from diagrams published earlier (7, 8).

If the dissolution efficiency is not known MB may be estimated from the lake chemistry. Use the calcium concentration before liming, and a value for calcium some time after the liming has been carried out, e.g. one or two months. The amount dissolved may then be approximated as DM:

$$DM = \frac{Ca^{2+}_{\text{After}} - Ca^{2+}_{\text{Before}}}{Y} * 2.5 * VL \quad (\text{tons}) \quad (66)$$

If the calcium concentrations are kept in mg/l and the lake volume, VL, in million m³, DM will be in tons of calcite. Y is the fraction of CaCO₃ in the calcite used, as natural calcites are seldom 100 % pure. Y would typically be 0.85-0.95.

The residual amount on the bottom may now be estimated as the total amount added minus the amount dissolved in the lake volume at the time of application:

$$MB = TM - DM \quad (67)$$

It can be seen from the reacidification nomograph that an increase in the amount on the bottom will increase the time required to reacidify the lake. But after a certain dose on the bottom has been obtained, additional increase in the amount on the bottom will produce progressively smaller increases in the reacidification time.

The reacidification diagram represents the projection of a multidimensional problem into the dimensions of three variables: the hydraulic residence time, the amount on the bottom and the bottom calcite cover P. It must be kept in mind that the diagram gives an estimation and a reasonable prediction based on a number of simplifications and assumptions. The use of the computerized reacidification model, however, will give a substantially more complete picture of the process of reacidification.

The reacidification model as a management tool - A case study

We will try to illustrate the use of the model with an example. The Lake Bredvatten was limed in 1974 with T-slag, a calcium silicate with dissolution kinetics similar to calcite under the conditions on the bottom of a lake. Bredvatten is a clear-water lake near Stenungsund on the Swedish West Coast. Its volume is 0.9 million m³, the

average depth is 3.4 m and the residence time 3.4 years. The reacidification of the lake until its reliming in 1981 was carefully monitored and reported by Hans Hultberg and I. Andersson (1979).

With the model we may simulate the reacidification of Lake Bredvatten, and also check the calculation against the observed data. In the actual liming, the lake was limed with 40 tons, of which 15 tons dissolved and 25 tons precipitated to the bottom. The result of the calculation is shown in figure 22.

Now we would like to ask some hypothetical questions: What if there had been a different amount of calcite on the bottom? How would that affect the time required to reacidify the lake? What would the cost per year be if the lake was to be kept at a pH-value above pH 6 for different amounts of calcite on the bottom?

We may run through a number of possibilities from zero to four times the actual amount on the bottom. As we want to keep the amount instantly dissolved in the water column constant, the hypothetical goal is achieved by using calcite powders of different grind. That implies that a very fine grinding grade will leave no calcite on the bottom, a coarse one will leave very much on the bottom.

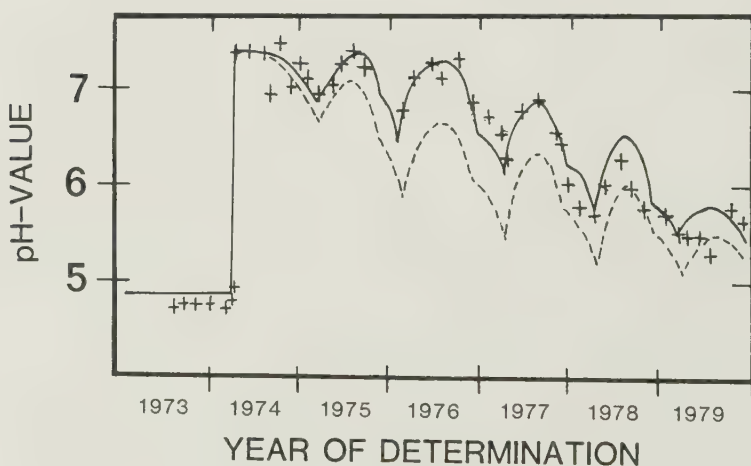


Figure 22

Reacidification model calculation for Lake Bredvatten near Göteborg. The drawn line uses the actual indata, the dotted line the case with no calcite on the bottom for comparison. Bredvatten has a residence time of approximately 2.4 years, a volume of 0.9 million m^3 and an average depth of 3.4 meters.

The crosses (+) indicate the observed values, the drawn line (—) the calculation with the model. The dotted line is a model calculation for the hypothetical case where there is no residual calcite on the bottom.

The results of our calculation is shown in table 8, listing the reacidification time for different amounts of calcite on the bottom. The current market prices for December 1984 were used and the yearly cost for keeping the lake at a pH above pH 6.0 is indicated. The most cost efficient alternative for keeping the lake Bredvatten above pH 6.0 can be identified as the one involving a modest dose on the bottom of the powder called 0-0.2 mm. For shallowed lakes the optimum will be pushed towards powders with a finer grinding grade, for lakes substantially deeper towards coarser powders.

Particle size distribution curve

	8	7	6	5	1
Commercial name of powder	0-0.044 mm	0-0.2 mm	0-0.5 mm	0-1 mm	0-3 mm
Amount required to neutralize the lake volume	15 tons	15 tons	15 tons	15 tons	15 tons
Amount on the bottom	3 tons	10 tons	25 tons	50 tons	100 tons
Total amount	18 tons	25 tons	40 tons	65 tons	115 tons
Price per ton applied, kr/ton	450	330	300	280	250
Calcite application cost, kr	8100	8250	12000	18200	28750
Fixed costs, kr	3000	3000	3000	3000	3000
Total cost, kr	11100	11250	15000	21200	31750
Bottom dose, ton/hectare	0.11	0.37	0.32	1.85	3.7
P-factor	0.05	0.10	0.10	0.20	0.3
B-factor, ton/hectare	0.03	0.19	0.46	1.85	5.5
Time required for reacidification to pH 6.0 years	2.7	3.3	4.4	5.3	6.0
Yearly costs for keeping the lake above pH 6.0	4110	3400	3750	4000	5300

Table 8 Calculation example for alternatives to the actual liming of Lake Bredvatten with 0-0.5 mm T-slag. The example shows how a reacidification model, either as a computer program or as reacidification diagrams, may be used to optimize lake liming operations

Coarser powders will require a larger dose compared to the powder called 0-0.2 mm, in order to obtain pH 7.0 in the lake volume, and the proportionally larger amount on the bottom will not increase the time required for a reacidification to the same extent. It becomes more cost efficient to relime with a modest dose of a fine ground material than to place large amounts on the lake bottom. The difference in cost may be substantial.

INITIATE LAKE LIMING PLANNING

Based on defined biological or chemical set standards, decisions are made whether a lake should be considered for liming or not



MITIGATION LOCALIZATION

Based on the target water chemistry as defined by biological and other requirements, the mitigation effort is localized somewhere in the system



SPECIFIC NEUTRALIZATION DEMAND

The specific neutralization demand is determined as an experimental titration curve

The specific neutralization demand is estimated from the water chemistry with some sort of model or the specific neutralization demand is estimated from water color



THEORETICAL NEUTRALIZATION AMOUNT

Based on the specific neutralization demand, lake volume as well as sediment neutralization requirement, the theoretical amount dissolved calcium carbonate in the system is calculated



ACTUAL APPLICATION DOSE

Based on system characteristics is the dissolution efficiency calculated with diagrams or model calculation, and hence the actual application amount



REACIDIFICATION

The result is calculated as achieved neutralization level and result duration and stability as well as the reacidification time



CONTROL

Consider if chemical water quality targets are met
Consider if biological water quality targets are met
Consider if duration and stability targets are met

If not all are positive, mitigation is relocalized



COST OPTIMIZATION

The possible mitigation alternatives are analysed for total cost and cost effectiveness in terms of cost per year above target values. The most cost effective is selected



INITIATE LAKE LIMING

4. A DOSE CALCULATION MODEL

Introduction

It is of importance when a liming project is planned that the decisions taken are adequate and proceed in the right order, as they depend upon each other. The flow-diagram tries to identify the most important steps and their order. In the recommended procedure the mitigation measure is localized somewhere in the system. Next the dose is calculated and dissolution models, reacidification models as well as hand calculations are used to control if the calculated dose will be able to produce the target values. The procedure is repeated for different alternatives. The last step is to calculate the cost-effectiveness for all viable alternatives and select the most attractive.

In this chapter we will go through the dose calculation for a lake liming step by step following the flow diagram.

Theoretical neutralization dose requirement

The amount of dissolved calcium carbonate required to raise the pH-value we will define as the specific neutralization demand (dN/dpH). It is somewhat dependent on the chemical composition of the water as well as the initial starting point. The safest way to determine the specific neutralization demand or the dissolved amount required to go from one pH-value to a determined target, the neutralization demand, is to titrate a sample with calcium carbonate. An example of a titration curve is shown in figure 23. The specific demand is represented by the slope of the curve.

The neutralization demand is defined as the amount dissolved required to raise the pH-value from a value pH_1 to a value pH_2 :

$$N = \int_{pH_2}^{pH_1} \left(\frac{dN}{dpH} \right) dpH \quad (g \text{ CaCO}_3/m^3) \quad (68)$$

A close study of titration curves such as the one in figure 1 shows that the titration curve is relatively straight between pH 4.5 and pH 6.5.

Lake neutralization usually takes place at pH-values between pH 4.5 and pH 6.5.

Accordingly if a titration curve cannot be determined we may assume (dN/dpH) to be constant in the pH-interval pH_2 to pH_1 and approximate the neutralization demand as:

$$N = \left(\frac{dN}{dpH} \right) * (pH_2 - pH_1) \quad (g \text{ CaCO}_3/m^3) \quad (69)$$

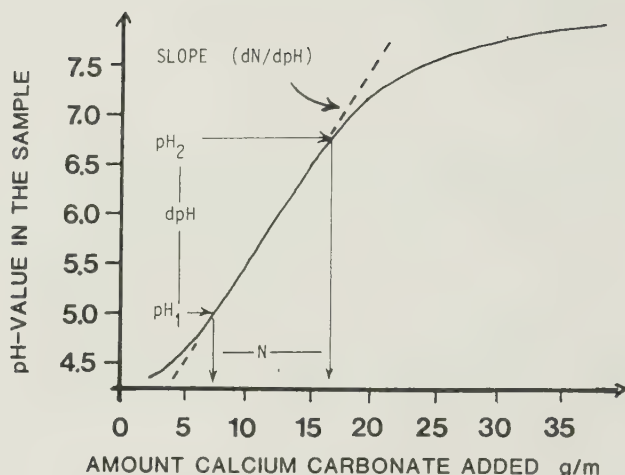


Figure 23

The best way to determine the neutralization demand of a water is to determine the titration curve. The neutralization need is defined as the amount of calcium carbonate that is required to raise the pH-value from the initial value to the defined target. The slope of the curve is called the specific neutralization demand and it is often constant, that is the curve is straight in the interval between pH 4.7 and pH 6.5.

It described the response in pH-value or alkalinity to additions of dissolved neutralizing agent and it is easy to determine.

The dose at dissolved calcium carbonate is calculated as the specific neutralization demand times the pH-elevation desired. The specific neutralization demand may be estimated as follows:

Water quality	Water colour	(dN/dpH)
Clear water	0- 20 mg pt/l	3-5 g CaCO_3/m^3 pH
Normal lake water	20- 60 mg pt/l	5-6 g CaCO_3/m^3 pH
Brown water	60-100 mg pt/l	6-7 g CaCO_3/m^3 pH
Very humic water	100-200 mg pt/l	7-9 g CaCO_3/m^3 pH

In the report 3/82 from the Norweigian liming Project (Wright 1982), a method for calculating the dose is suggested. The method is based on alkalinity and requires data for aluminium. In Sweden lakes with brown water, iron may be as important as aluminium for determining the dose. Accordingly we have modified the calculation procedure. The amount alkalinity needed is added together for different tasks.

Neutralization of hydrogen ions	mekv $\text{HCO}_3^-/1$
Increase of the alkalinity to target level	mekv $\text{HCO}_3^-/1$
Neutralisation of Al^{3+} 0.12 mekv HCO_3^- per μg Al^{3+}	mekv $\text{HCO}_3^-/1$
Neutralization of Fe^{3+} 0.06 mekv HCO_3^- per μg Fe^{3+}	mekv $\text{HCO}_3^-/1$
Neutralization demand N as alkalinity	mekv $\text{HCO}_3^-/1$

The determined amount is then converted to calcium carbonate by assuming that 1 g CaCO_3 will give 0.02 mekv HCO_3^- .

The total theoretical amount calcium carbonate for a lake or a lake segment is determined as the volume times the neutralization demand.

$$\text{MT} = \text{N} * \text{V} \quad (\text{ton } \text{CaCO}_3) \quad (70)$$

If N has the units g CaCO_3/m^3 and the volume V million cubic meter, MT, the total theoretical amount, will be in metric tons.

The actual neutralization dose

Most calcite powders will, depending on their grinding grade, dissolve partially. In order to compensate for this the dissolved fraction must be known. Calcite as a mineral is usually rather pure calcium carbonate, however, not completely. Hence all mass that dissolves is not capable of neutralizing the acid, and this must be considered.

The fraction neutralizing solids in the mineral will either be given as percent CaCO_3 or percent CaO. The fraction Y may be calculated as

$$\text{Y} = \text{percent } \text{CaCO}_3 / 100 \quad (71)$$

or

$$\text{Y} = \text{percent } \text{CaO} * 0.0178 \quad (72)$$

The dissolved fraction X may be determined with diagrams such as presented earlier or by model calculation. The actual neutralization amount may be calculated as

$$\text{MA} = \frac{\text{MT}}{\text{X} * \text{Y}} \quad (\text{ton calcite}) \quad (73)$$

or in terms of measured and estimated variables

$$\text{MA} = \frac{\text{V} * \text{N}}{\text{X} * \text{Y}} \quad (\text{ton calcite}) \quad (74)$$

or

$$\text{MA} = \frac{\text{V} * \left(\frac{d\text{N}}{d\text{pH}} \right) * (\text{pH}_2 - \text{pH}_1)}{\text{X} * \text{Y}} \quad (\text{ton calcite}) \quad (75)$$

For larger dosages above 25-30 g/m³ the figures for the dissolved fraction will have to be corrected for the higher dosage. This is automatically done in the computer model by calculation of the parameter B as well as the effect of disappearing chemical driving forces on the dissolution as the saturation concentration is approached. Figure 8 shows a diagram based on experimental determination of the effect. By entering the diagram with the dose calculated without considering the size of the dose, the factor RX may be determined, by which the dissolution efficiency X must be reduced (Sverdrup & Warfvinge 1985).

In such a case we get

$$MA = \frac{V * N}{X * RX * Y} \quad (\text{ton calcite}) \quad (76)$$

Sediment neutralization

The sediments of acid lakes will become acidic as well as base cations are leached the sediments and exchanged for hydrogen ions. After liming, as the calcium concentration in the water column is increased, calcium will be adsorbed to the sediments and exchanged for hydrogen ions. Accordingly, sediment not receiving a sufficient amount of residual calcite after liming will work as a sink for calcium and accordingly alkalinity (Sverdrup & Warfvinge 1984).

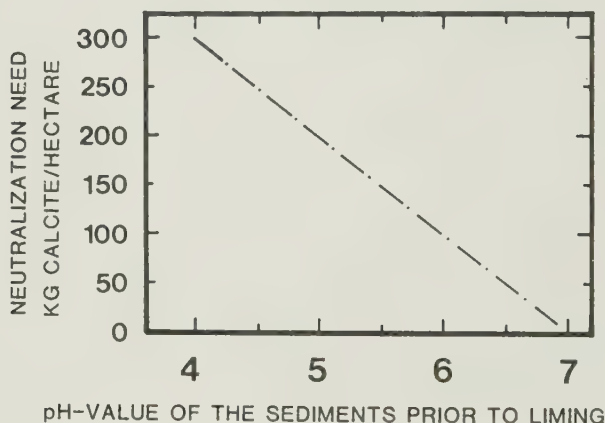


Figure 24

The sediments of an acid lake will become acid as well, and after liming be capable of consuming calcium ions in exchange to hydrogen ions. The diagram to estimate the sediment need was based on titrations on sediments from the lakes in the Härskogen area (Hultberg et al 1979) as well as sediment neutralization requirements determined in the LAMP project by DePinto (1985). The diagram is consistent with expressions used to estimate the ion exchange capacity of soils as well (Sverdrup & Warfvinge 1985).

The amount needed to neutralize the upper sediment layers may easily be determined by titration. Such titration are however seldom carried out in operational liming. The neutralization dose may be estimated from the assumption that 75-100 kilogram calcite per hectar and pH-unit is required. The assumption is based on titrations on lake sediments from the Göteborg region (Alenäs et al 1982) and supported by information presented by DePinto et al (1982) and Molot et al (1985), as well as by theoretical considerations developed for soil neutralization (Sverdrup & Warfvinge, 1985). The amount per hectar may be read from the diagram shown in figure 24.

The total amount required for the neutralization of the sediments is given by:

$$MS = A * BS * 0.80 \quad (77)$$

BS is the demand taken from figure 24, A the lake surface area. The factor 0.80 accounts for the assumption that the lake bottom is on the average covered by sediments in 80 % of the area.

The minimum amount to be applied in a lake liming should be sufficient to both neutralize the sediments and the water column.

Calcite powders regularly used for lake liming (Nos. 5, 6, 7, 8) generally dissolve partially, having a substantial amount on the bottom. However, it must be checked if this amount is sufficient to neutralize the sediments. The criterion may be expressed as:

$$MA * (1 - X) > MS \quad (78)$$

If the criterion above is done, then the calcite amount precipitated will suffice to neutralize the sediments. The total amount to be applied will be the amount required to neutralize the water column.

$$MMIN = MA \quad (79)$$

If a very small amount is precipitated to the bottom, it may not suffice to neutralize the sediments and an additional amount must be added to the dose. The total amount to be applied becomes:

$$MMIN = MA * X + MS \quad (80)$$

or

$$MMIN = MT + MS \quad (81)$$

Thus is the minimum dose defined required to produce a result close to the predetermined target value. The maximum dose is the amount needed to neutralize the water column plus the maximum amount that may dissolve of a lake bottom as indicated in table 4. If the amount indicated in table 4 is called MX we get:

$$MMAX = MA * X + MX \quad (82)$$

The reasonable dose for a lake liming will be found between the limits MMIN and MMAX.



For the fiscal year 1985/1986 the Swedish Parliament budgetted 90 million Swedish Kronor, equal to more than 10 million US Dollars or 35 million German Marks. Although there is a vast number of small liming projects, will a substantial number be involving large sums of money. Lake liming projects such as the liming of Lake Stora Le, a total of 9000 tons, or the liming of Lake Udden, a total of 9000 tons, or the liming and re-liming of the Kornsjö-Boksjö system, in portions of 6000 tons, calls for efficient planning of all steps involved, ranging from finacial planning to organizing a fleet of trucks to supply the operation at the lake.

5. LAKE NEUTRALIZATION COSTS

Considering costs of lake liming

It will be of importance to evaluate and study the economics of neutralization as soon as liming is carried out to operational projects. Very often several alternative methods or strategies will have the capability of producing the desired result but the costs involved may vary considerably.

The main design variable influencing the cost will be the grinding grade which influences the material cost and the amount of material. Accordingly such projects where the cost of calcite is a main part of the total project cost, will be able to profit from cost optimization.

An accurate neutralization calculation and cost optimization will generally be able to reduce the project costs by 15-30 % as compared to the simplified procedure recommended by the Swedish Environmental Protection Board (SNV). Optimization is well paid for in projects larger than a total cost of 50 000 kronor if it is assumed that 10 000 kronor is spent on detailed technical planning and cost optimization. Cost optimization is not economical for smaller projects.

In the provinces of Sweden which are most affected by acidification several million kronor are budgetted each year for liming. Between one half and one third of all these projects involve costs in excess of 50 000 kronor. By systematic technical planning and economical optimization it should be possible to save 20-30 % of the costs or correspondingly increase the volume of liming carried out.

Optimization variables and liming costs

In order to be able to compare costs it will be necessary to define cost effectiveness. In a first approach this was defined as cost per ton calcite dissolved, CTD.

$$CTD = \frac{\text{Amount dissolved}}{\text{Total project cost}} \quad (83)$$

The cost effectiveness is a powerful test for optimizing the cost of neutralizing a water column from an initial state to a defined target value when different neutralizing agents are used as well as grinding grades.

The total project cost is the sum of the material cost, costs for transportation, cost for application and the cost of establishment of equipment at the lake as well as design costs.

$$\text{TOTAL COST} = \text{MATERIAL} + \text{TRANSPORT} + \text{APPLICATION} + \text{EXTRAS} \quad (84)$$

Commercial namn	Part size distr no	Material cost	Transportation cost	Application cost	Sum
Aglime	5	80	100	100	280
0-0.5 mm	6	100	100	100	300
0-0.2 mm	7	130	100	100	330
0-0.5 mm	8	250	100	100	450
Filler Chalk	9	350	125	125	600
Filler marble	10	400	125	125	650

Table 9 Cost for boat application lake liming for different calcite powder grinds. For powder nos. 9 and 10 a higher cost for transportation and application was assumed as they are delivered as slurries containing approximately 30 % water. The material costs are based on actual costs for 1984 as given by Sweden's three major calcite quarries

Commercial namn	Part size distr no	Material cost	Transportation cost	Application cost	Sum
Aglime	5	80	100	300	480
0-0.5 mm	6	100	100	300	500
0-0.2 mm	7	130	100	300	530
0-0.5 mm	8	250	125	350	725
Filler Chalk	9	350	125	350	825
Filler marble	10	400	125	350	875

Tabell 10 Cost of liming in kr/ton for aircraft application. The actual application cost is assumed, the material cost based on actual prices on the Swedish market in 1984. 300 kr for air application is taken as an example. The application cost may vary substantially however from 280 to 1000 kronor per ton

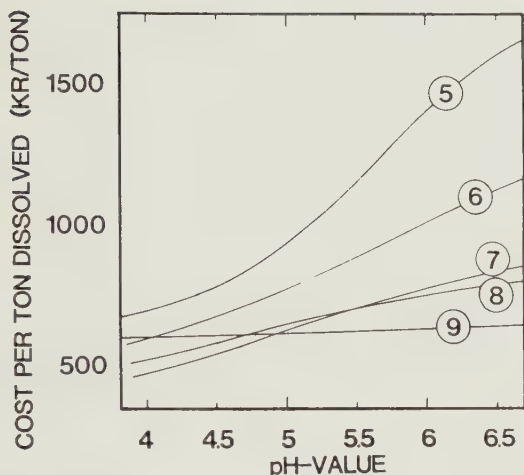


Figure 26

The cost per dissolved ton is a powerful optimizing variable if neutralization of the water column only is considered. This is relevant for lakes with very long retention times where residual dissolution is unimportant and in stream liming. Based on the dissolution efficiency from figure 9 and the prices outlined in table 9, the diagram may be made.

For the powders usually used in Sweden we may make tables for boat application and for aircraft application.

The information in table 9 and 10 may be used to optimize the cost of neutralizing the water column such as shown in figure 26 when the actual cost per ton dissolved is calculated as function of initial pH for each grinding grade of calcite.

In lakes, however, the cost per dissolved ton does not consider all factors, especially when cases of different degree of neutralization are compared. A redefinition of a cost optimization variable is needed. In a lake liming certain target values are defined in terms of minimum pH-value and alkalinity before reliming is required. So what we really want to know is the cost for staying above the minimum requirements per time unit. This could be defined as the yearly neutralization cost, YCN:

$$\text{YCN} = \frac{\text{Total project cost}}{\text{Reacidification time}} \quad \text{kr/yr} \quad (85)$$

With this variable we may compare all kinds of alternatives which meet the target value requirements, regardless of how it is achieved.

A case study, lake Stora Neden

To illustrate how cost optimization is carried out, we will show how this was carried out in the case of lake Stora Neden, in the Province of Halland.

Stora Neden has a volume of 60 million cubic meter, in deep, the average depth is 20 meter, maximum is 60 meter. Prior to liming the pH-value of the lake was pH 4.7-4.9. The hydraulic retention time of the lake is 7 years.

Following the procedure outlined in the earlier chapters, the amount of calcite required to neutralize the lake to pH 7.0 was calculated for several different grinding grades. The lake was segmented and a bathymetric map was used for the calculations (Sverdrup et al 1985). The required amounts are shown in table 11.

Commercial name	Size distr curve no	X %	Amount tons
Agricultural limestone	5	33	1980
0-0.5 mm	6	45	1450
0-0.2 mm	7	59	1120
0-0.05 mm	8	77	852
Filler chalk	9	100	700
Filler marble	10	100	700

Table 11 The amounts required for the lake Neden if different grinding grades are used. X represents the predicted dissolved fraction during sinking. It was assumed neutralization of the lake to pH 7.0. As the last two powders dissolve completely, the requirements of the sediments have been added to the dose, ca 45 tons

The costs per ton calculated in table 9 and 10 were used to calculate the total project costs. An additional cost for planning and establishment on the lake location of 5000 kronor was assumed.

Both liming from boat and from aircraft were considered. Aircraft application is often the only alternative when remote lakes are to be limed. The total costs for both alternatives are summarized in table 12.

With the reacidification model described earlier we may estimate the reacidification time. In table 13 we have also calculated the hypothetical reacidification time for a lake as Stora Neden with retention times of 1 or 2 years.

Commercial namn	Size distr curve no	- Total project cost -	
		Boat application	Aircraft application
Agricultural limestone	5	554 000	1 022 000
0-0.5 mm	6	440 000	906 000
0-0.2 mm	7	370 000	813 000
0-0.05 mm	8	380 000	623 000
Filler chalk	9	425 000	578 000
Filler marble	10	460 000	613 000

Table 12 Total costs for boat application as well as air-drop. For aircraft application it was assumed that nos. 8, 9 and 10 were applied as wet slurries. For the other powders the amount were increased to compensate for the lower dissolution efficiency due to dry application, corresponding to the fract of the powder with mean diameter less than 6 microns, no. 6 had 20 %, no. 7 had 27 %, no. 8 had 40 % less than 6 microns. For powders finer than 9 the reduction of the dissolution efficiency were assumed to be 50 %

Commercial name	Size distr curve no	Reacidification time to pH 6.0		
		T=1 yr	T=2 yr	T=7 yr
Agricultural limestone	5	2.5	4.5	9.5
0-0.5 mm	6	2.4	4.2	9.5
0-0.2 mm	7	2.2	4.0	9.0
0-0.05 mm	9	1.7	2.8	7.5
Filler marble	10	1.7	2.8	7.5

Table 13 The time required to reacidify the lake to pH 6.0 when it is limed with the amounts indicated in table 11. The values were determined with the reacidification model for a lake like Stora Neden, assuming the residence time of the lake to be 1, 2 and 7 years

With the information presented in tables 12 and 13 the yearly cost of keeping the lakes above the reacidification limit may be calculated as defined

$$\text{YNC} = \frac{\text{Total project cost}}{\text{Reacidification time}} \quad \text{kr/yr} \quad (86)$$

For boat application, the yearly cost is shown in table 14 for lakes such as Stora Neden with a retention time of 1, 2 or 7 years. The same calculations have been repeated for aircraft liming, the figures are listed in table 15.

Commercial name	Size distr. curve no	YNC (1000 Kronor/year)		
		T=1 yr	T=2 yr	T=7 yr
Agricultural limestone	5	222	110	52
0-0.5 mm	6	183	105	46
0-0.2 mm	7	171	92	41
0-0.05 mm	8	204	110	45
Filler chalk	9	250	152	56
Filler marble	10	270	164	61

Table 14 The yearly neutralization cost YNC for the lake when limed from boat. Powder no. 7 may be identified as the most cost efficient. T is the hypothetical residence time of the lake

Commercial name	Size distr. curve no	YNC (1000 Kronor/year)		
		T=1 yr	T=2 yr	T=7 yr
Agricultural limestone	5	408	230	108
0-0.5 mm	6	378	216	95
0-0.2 mm	7	370	203	90
0-0.05 mm	8	325	170	73
Filler chalk	9	340	206	77
Filler marble	10	360	245	81

Table 15 The yearly neutralization cost YNC for the lake when limed from an aircraft. Powder no. 8 may be identified as the most cost efficient. The costs are in units thousand. T is the hypothetical residence time of the lake

Commercial name	Size distr curve no	(1000 Kroner/year)	
		Dry	Wet
Agricultural limestone	5	108	116
0-0.5 mm	6	95	87
0-0.2 mm	7	90	77
0-0.50 mm	8	123	73
Filler	9	140	77
	10	149	81

Table 16 A comparison of wet slurried aircraft application to drydrops for lake Stora Neden. Even when the increased cost for transportation and application of 25 % water is included, wet slurried airdrop will be the most cost effective alternative

The information in table 14 and 15 stress the point that liming by boat will always be less costly compared to aircraft application, as long as the lake has some access.

The tabulated values show that for boat application in a lake like Stora Neden will powders with a size distribution curve equal to 7, called 0-0.2 mm be cost optimal. This is however moved towards finer grinding grades as the application costs increase.

By performing a number of cost studies as the one demonstrated for Stora Neden, a more general picture of lake neutralization costs may be formed.

We could in this way identify a number of parameters which will influence the position of the economical optimum, and in which direction it will be changed.

The following parameters will move the economical optimum with respect to the grinding grade of the calcite powder towards more finely ground powders:

- High initial pH-value
- Small sinking depth
- High dosage, above 20-30 g/m³
- Liming over a very small fraction of the lake surface area
- High application cost
- Dry powder application

The factors mentioned above will contribute to a reduction of the fraction dissolved and accordingly an increase in neutralization costs.

Several factors may make the optimal powder be a powder coarser than no. 7, 0-0.2 mm.

- Low initial pH-value
- Great sinking depth
- Low dose
- Low application cost

In figure 27 the position of the optimum has been related to the cost of application, in terms of optimal grinding grade. It may be seen that the optimal powders for boat application will generally be such powder as nos. 6 and 7. However for aerial application such powders as nos. 8 and 9 will be most cost efficient.

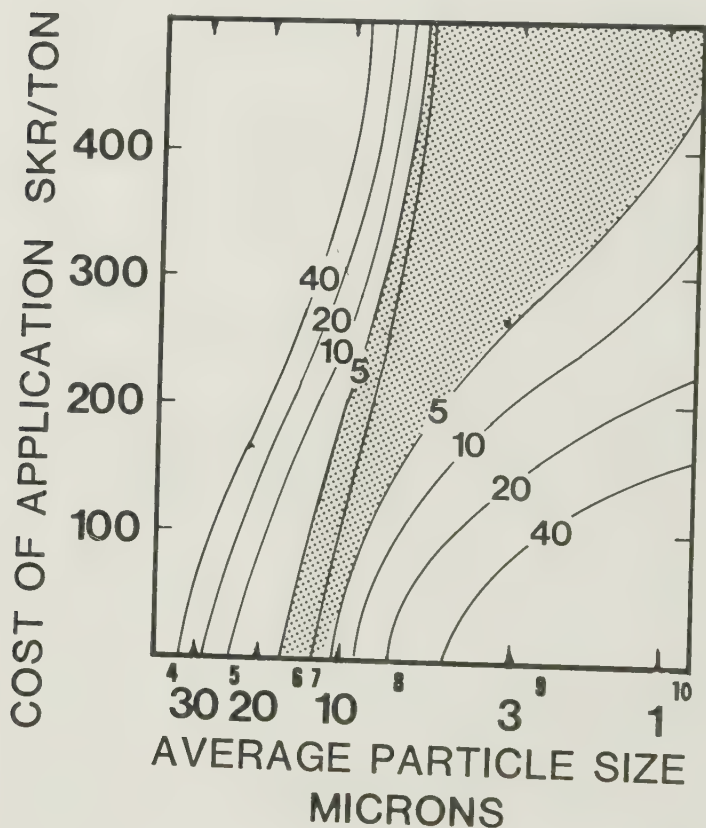


Figure 27

The position of the optimal calcite powder grinding grade as a function of spreading costs. The lines indicate the percentual increase in costs in comparison to the optimum, induced by choosing something different from the optimal grinding grade.

The diagram applies to a lake with initial pH-value in the range pH 4.7-5.2 and a depth of 5-20 meter. A smaller depth or a higher pH-value will move the optimum towards finer powders. A lower pH-value or greater depth will move the optimum towards coarser powders. The optimal cost is defined as the lowest cost per year for keeping the lake above the reliming point.

6. ACKNOWLEDGEMENTS, NOTATION, REFERENCES, E.T.C.

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Throughout the work (1980-1985) I enjoyed many interesting discussions with my fellow colleagues, as well as received constructive criticism, Dr. Hans Eklund, Dr. Hans Karlsson and Tekn.Lic Per Warfvinge.

To have the results of one's reseach applied in real life is a privilege for a scientist. Sven Erlandsson and his associates at Cementa AB in Malmö provided us with many chances to test methods and principles in full scale on short notice. The contact with Cementa AB provided us valuable insight into industrial operational liming.

Bo Bengtsson at the Swedish National Board of Fisheries, have been of great help throughout the work. Through him we have been able to draw upon the information in the archives of the Swedish Experimental Liming Program (1977-1981). During my frequent visits in Göteborg, he also proved to be an excellent host.

Many companies and agencies have contributed to this thesis; The Research Fund of Euroc provided funding for two years of research by a donation to the University. Further support were provided by Cementa AB, Malmö, Kedjeteknikk AB, Malmö, Sydkraft AB, Malmö, Tennessee Valley Authority, Knoxville, Ontario Ministry of the Environment, Toronto, as well as the Ground Water Acidification Mitigation Project at the Swedish Environmental Protection Board, Stockholm.

SYMBOLS

A	Collection of many constants into one	
A'		
A _L	Lake surface area	(m ²)
A _S	Mineral surface area	(m ²)
B	Dose load factor	(ton/ha)
BS	Sediment neutralization requirement	(ton/ha)
D	Diffusivity	(m ² /s)
CM	Amount dissolved during sinking	(ton)
CTD	Cost per ton dissolved	(kr/ton)
g	Gravitational acceleration	(m ² /s)
i, j	Index	
K	Rate constant	
K1	Rate constant, reaction with the hydrogen ion	
K2	Rate constant, reaction with carbon-dioxide	
KW	Rate constant, reaction with water	
KB	Rate constant, backward reaction rate	
K _I	Selectivity coefficient	
K _{II}	Selectivity coefficient	
KH	Deactivation rate	(yr-1)
KH ₀	Infinite deactivation limit	
KM	Mass transfer coefficient	(m/s)
KA	Absorption coefficient	
m	Mass	(ton)
m ₀	Initial mass	(ton)
M _E	Conversion factor from kg to kmol	(kg/kmol)
MT	Theoretical dose	(ton)
MA	Actual dose, sediments not considered	(ton)
MMIN	Minimum total application dose	(ton)
MMAX	Maximum total application dose	(ton)
MS	Theoretical dose for the sediment	(ton)
MB	Amount on the bottom	(ton)
n _i	Reaction order	

N	Neutralization dose	(g/m ³)
P	Fraction of the bottom with full calcite cover	(%/100)
Q	Flow rate	(m ³ /s)
V	Lake volume	(m ³)
RT	Reaction rate	(kmol/m ² s)
r	Radius	(m)
r ₀	Initial radius	(m)
r	Boundary layer thickness	(m)
R _C	Calcite reaction rate	(kmol/m ² s)
R _D	Dolomite reaction rate	(kmol/m ² s)
Re	Reynolds number	
S	Depth	(m)
Sc	Schmidt number	
SA	Sorbed amount	(ton/ha)
SM	Sorption capacity	(ton/ha)
t	Time	(s)
TM	Total amount added	(ton)
T	Retention time	(yr)
Y	Calcium carbonate content of the calcite	(%/100)
YNC	Yearly neutralization cost	(kr/yr)
X	Dissolved fraction	(%/100)
α	Reaction rate	(kmol/m ² s)
α ₀	Initial reaction rate	(kmol/m ² s)
α _t	Reaction rate at time t	(kmol/m ² s)

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III. SELECTED PUBLISHED WORKS

DISSOLUTION OF CALCITE AND OTHER RELATED MINERALS IN ACIDIC AQUEOUS SOLUTION IN A pH-STAT

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Abstract

Experiences from the lake and soil liming program has clearly shown that a knowledge of the mechanisms of calcite dissolution is essential to avoid waste of time and effort.

It is the intentions of this report to present a diffusion model for the dissolution of calcite in natural waters, based on experiences from our own experiments and that of others. We include a dissolution study of other minerals used in lake liming, so that a basis can be offered for comparing the different minerals used in lake liming operations. Mathematical expressions are given which can serve as building blocks in dissolution calculation for calcite.

With a pH-stat apparatus the mass transfer rates and dissolution rates were measured for calcite, olivine, dolomite, slaked lime and soda. The dependence of these rates upon particle size, pH-value of the solution and CO_2 were determined.

Introduction

Thousands of lakes and rivers in Scandinavia and North America located on low weathering bedrock or surrounded by soils with a low calcite content are suffering from the effects of acid rain.

In Norway and Sweden waters in the southern parts of the countries, an area of almost 200,000 km^2 , will have critical pH-values during some time of the year. Some forty thousand lakes are affected, in addition to countless kilometers of rivers and brooks.

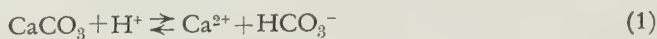
The measure most frequently taken is applying limestone in different ways to the river or lake affected. This is in fact the only large scale remedy available until emissions of SO_2 and NO_x have been reduced drastically on the European continent.

In Sweden large programs for liming of lakes are under way and about 200 million Swedish kronor will be spent each year in the final program. In southern Sweden the total amount needed for neutralization of the acid precipitation reaches 800,000 tons of calcite each year. It is obviously of great importance to use the limited resources efficiently, in order to repair as much as possible. Alas, knowledge of the processes involved is necessary to achieve satisfactory results without excessive costs.

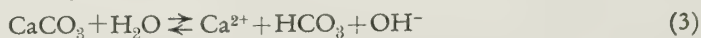
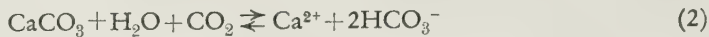
The dissolution of solid calcite in dilute acid can be described as a heterogeneous solid-liquid reaction. It can readily be described with mass transfer models following the

principles outlined by Sherwood et al. (1) and Crank (2). The intentions of this study is to present a mass transfer model for the dissolution of calcite in dilute acid and lake water.

The chemical reaction of calcite with acid can be written



At low pH-values this reaction will dominate over the two alternatives in aqueous solution which are



These reactions play a role at low concentrations of H^+ only or at high CO_2 partial pressures.

The dissolution process comprises two steps governing it. The first of the two implies the transport of reactants from the bulk of the liquid into the reaction interface by diffusion. The second is the chemical reaction at the interface, usually the solid particle surface. The slowest step will control the total rate of the process.

For this model it is assumed that for the case of calcite, the mass transfer step is limiting. It is also assumed that diffusion takes place from the bulk of the liquid to the solid surface through a boundary layer. The thickness of this boundary layer depends on the hydrodynamic conditions around the particle.

For the dissolution of calcite in acid we have hydrogen ions diffusing into the solid surface, there to produce two ions, one of calcium and one of hydrocarbonate. Both these ions occupy more space than the hydrogen ion, and consequently we have a slow flux of volume outwards. The hydrogen ions are virtually diffusing upstream a flux of ions.

For the mass balance this means a mass transfer by diffusion inwards and diffusion in addition to volume flux outwards. Accordingly a correct mass balance has to take into account the effect of transpiration.

A mass balance considering the diffusion of all species involved does not add much accuracy compared to a simpler model involving the main diffusing species only. As the experiments will show, a model considering the diffusion of hydrogen ions alone will produce a concentration gradient around the particle, which makes the theory fit the experimental data well for dissolution in natural lake water between pH 2.0 and pH 6.5.

Theory

The mass balance around a sphere gives the general equation for diffusion from a sphere:

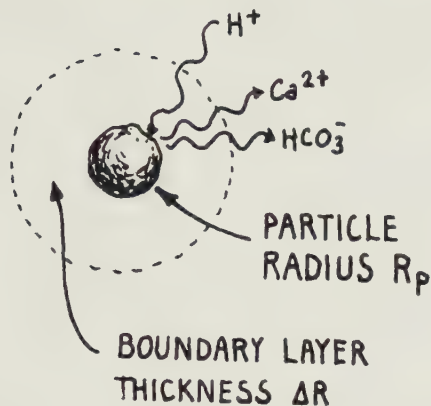
$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial R^2} + \frac{2}{R} \frac{\partial C}{\partial R} \right) \quad (4)$$

The consumption of mass from the sphere will be:

$$-\frac{\partial M}{\partial t} = D \left(\frac{\partial C}{\partial R} \right)_{R_p} A \cdot M_E \quad (5)$$

It is assumed that we have a state of pseudo steady state and therefore no accumulation in the boundary layer:

$$\frac{\partial C}{\partial t} = 0 \quad (6)$$



The boundary conditions are:

$$\left. \begin{array}{l} R = R_p \\ C = C_K \end{array} \right\} \quad \left. \begin{array}{l} R = R_p + \Delta R \\ C = C_L \end{array} \right\} \quad (7)$$

Equation (4) can be solved to give for the concentration gradient at the surface:

$$\left(\frac{\partial C}{\partial R} \right)_{R_p} = \left(\frac{dC}{dR} \right)_{R_p} = (C_L - C_K) \frac{R_p + \Delta R}{R \cdot \Delta R} \quad (8)$$

and when this is inserted in (5) we get:

$$-\frac{dM}{dt} = D \left(\frac{1}{\Delta R} + \frac{1}{R_p} \right) A \cdot (C_L - C_K) \cdot M_E \quad (9)$$

By substituting in eq. (9) with;

$$A = \frac{3 \cdot M}{R \cdot \rho} \quad (10)$$

$$R = R_o \cdot \sqrt[3]{\frac{M}{M_o}} \quad (11)$$

$$\Delta C = C_L - C_K \quad (12)$$

eq. (9) becomes:

$$-\frac{dM}{dt} = \frac{3 \cdot \Delta C \cdot M_F}{R_o \cdot \rho_p} \left(\frac{D}{\Delta R} M^{2/3} M_o^{1/3} + \frac{D}{R_o} M^{1/3} M_o^{2/3} \right) \quad (13)$$

with the boundary conditions:

$$\left. \begin{array}{l} t = 0 \\ M = M_o \end{array} \right\} \quad (14)$$

The general solution is;

$$1 - \frac{R}{R_o} + \frac{\Delta R}{R_o} \ln \left(\frac{R + \Delta R}{R_o + \Delta R} \right) = \frac{D \cdot \Delta C \cdot M_F}{R_o \cdot \Delta R \cdot \rho_p} \cdot t \quad (15)$$

The thickness ΔR of the boundary layer for a sphere is given by Sherwood et al. (1);

$$\Delta R = R_p \cdot \frac{1}{1 + 0.3 Re^{1/2} \cdot Sc^{1/3}} \quad (16)$$

For spheres in the state of free fall through a liquid this expression stays nearly constant for particle sizes ranging from a radius of 10 microns up to at least 400 microns. Eq. (16) is based on the mass transfer coefficient being equal to (17):

$$K_M = \frac{D}{\Delta R} \quad (17)$$

Thus, if the particle radius rises above 10 microns the ΔR will stay nearly constant. We get:

$$\frac{1}{\Delta R} + \frac{1}{R} \rightarrow \frac{1}{\Delta R}$$

and the resulting limiting case of eq. (15):

$$1 - \left(\frac{M}{M_0} \right)^{1/3} = \frac{K_M \cdot \Delta C \cdot M_E}{R_0 \cdot \varrho_p} \cdot t \quad (18)$$

which then describes the dissolution of spheres with a radius larger than 10 microns. For smaller particles we get;

$$\frac{1}{\Delta R} + \frac{1}{R} \rightarrow \frac{1}{R}$$

which gives the limiting case of eq. (15) for particles smaller than a radius of 10 microns:

$$1 - \left(\frac{M}{M_0} \right)^{2/3} = \frac{D \cdot \Delta C \cdot M_E}{R_0^2 \cdot \varrho_p} \cdot t \quad (19)$$

This also corresponds to the dissolution of a particle of any size in a stagnant medium. The transition point at 10 microns depends on the size of the turbulent eddies in the stirred liquid and their effect upon the boundary layer. It can therefore be influenced by stirring.

If we consider other minerals than calcite, olivine for instance, it can be seen that the chemical reaction on the surface is slower than the diffusion process. In this case the process is controlled by the chemical reaction rate per reaction surface area. The consumption of mass from the particle can then be written:

$$-\frac{dM}{dt} = K_R \cdot C_s^m \cdot C_L^n \cdot M_E \cdot A \quad (20)$$

where m and n depends on the reaction stoichiometry. Or:

$$-\frac{dM}{dt} = \frac{3K_R \cdot C_s^m \cdot C_L^n \cdot M_E}{R_0 \cdot \varrho_p} \cdot M^{2/3} M_0^{1/3} \quad (21)$$

which can be integrated to give:

$$1 - \left(\frac{M}{M_0} \right)^{1/3} = \frac{K_R \cdot M_E}{R_0 \cdot \varrho_p} \cdot C_s^m \cdot C_L^n \cdot t \quad (22)$$

As for the dissolution process we define the surface dissolution rate to be;

$$\left(\frac{\partial^2 M}{\partial A \partial t} \right) = K_R \cdot C_s^m \cdot C_L^n \quad (23)$$

where K_R is the chemically or mass transfer determined rate constant. C_s is the solid

concentration and C_L , the concentration of reactant for a diffusion process. We get;

$$\left(\frac{\partial^2 M}{\partial A \partial t}\right) = K_M \cdot \Delta C^n \quad (24)$$

with help of the logarithm of (24), K_M and n can be measured, n being the process order;

$$\ln \left(\frac{\partial^2 M}{\partial A \partial t}\right) = n \cdot \ln(\Delta C) + \ln K_M \quad (25)$$

A plot of the logarithm of the dissolution surface rate versus the logarithm of the reactant concentration or gradient, will have the mass transfer coefficient or the chemical reaction rate as intercept and process order as slope.

Experiment

The dissolution process was studied with a pH-state. The pH-state comprises a pH-meter, a regulating unit, an autoburette and a graphic recorder. It is possible to maintain a preset pH-value in a reaction vessel. If we study the dissolution of calcite, we find that the acid consumed and neutralized is automatically replaced and recorded. As the dissolution proceeds, the used amount of acid is recorded and thereby also the consumption of neutralizing mineral too.

Runs were made with particles of different distinguished size fractions. The separation of the fractions has been done with standard sieves. It is of great importance when the separation is done, that this is done wet with water. Smaller particles adhere to the surface of the larger particles and will not be separated from these during dry separation. This means that a dry fraction 90—100 μm in fact rather should be classified as 0—100 μm . The impact of this fact on the measurements should be obvious. The difference can be clearly seen in the Fig. 1 to 4, where the two first represent dry separation and the other two the wet separation method, where the particles were washed through the sieves with water.

The dissolution has been studied in a stirred tank where the particles were uniformly distributed throughout the liquid, and could be regarded as in a state of free fall. The experiments were designed to test the different parameters separately. The dissolution rate was studied in relation to particle size and surface area, hydrogen ion concentration, iron and aluminium content in the water, humus content in the water and magnesia in the calcite. The investigation was concentrated on the effects of particle size and hydrogen ion concentration. The acid used in the experiments was sulfuric acid. The minerals tested were calcite, olivine and dolomite, and slaked lime for comparison. The particle fractions used were produced by wet sieving for those with particles larger than 10 microns, and by sedimentation for those with smaller particles. The first category ranged from 0.4 mm to 0.010 mm, and the second from 10 microns to about 0.1 microns. Particles ranging from 10 microns to 400 microns in diameter have dissolution rate proportional to the particle diameter if the pH-value is kept constant. This can be seen in Figures 8—10 for calcite, olivine and dolomite. The curves showing remaining diameter versus time or $1 - (M/M_0)^{1/3}$ versus t are accordingly straight lines. This is also seen in Fig. 6.

The observed data agree very well with the predictions of the theory. In Table 1 the particle diameters and the correlation coefficient for the data are listed.

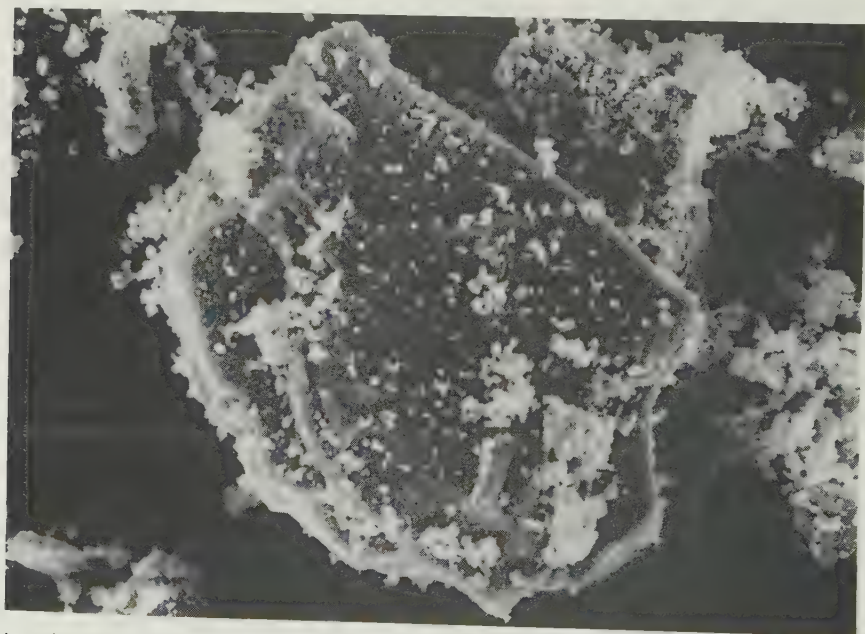
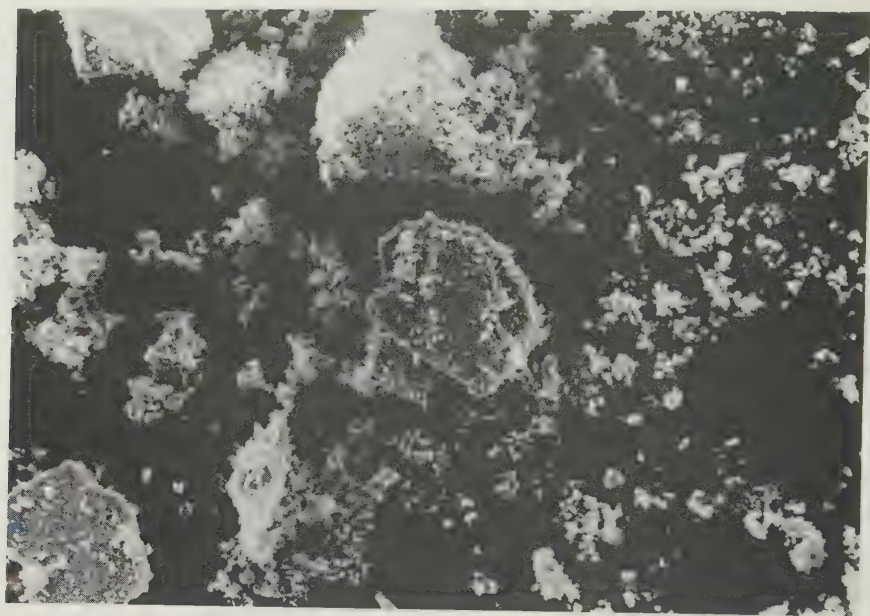


Fig. 1 and 2. The photographs were made with a scanning electron microscope and show a fraction obtained as 90—100 microns after sieving in dry condition. The magnification is 600 $\times$ and 200 $\times$. It can clearly be seen that the obtained fraction contains a large amount of smaller particles which adheres to the surface of larger particles. The fraction should rather be named 0—100 microns.

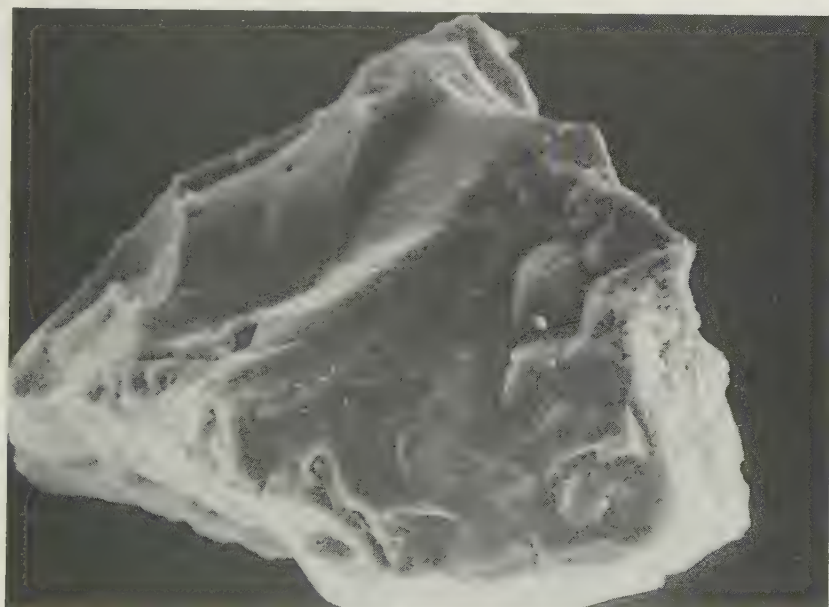
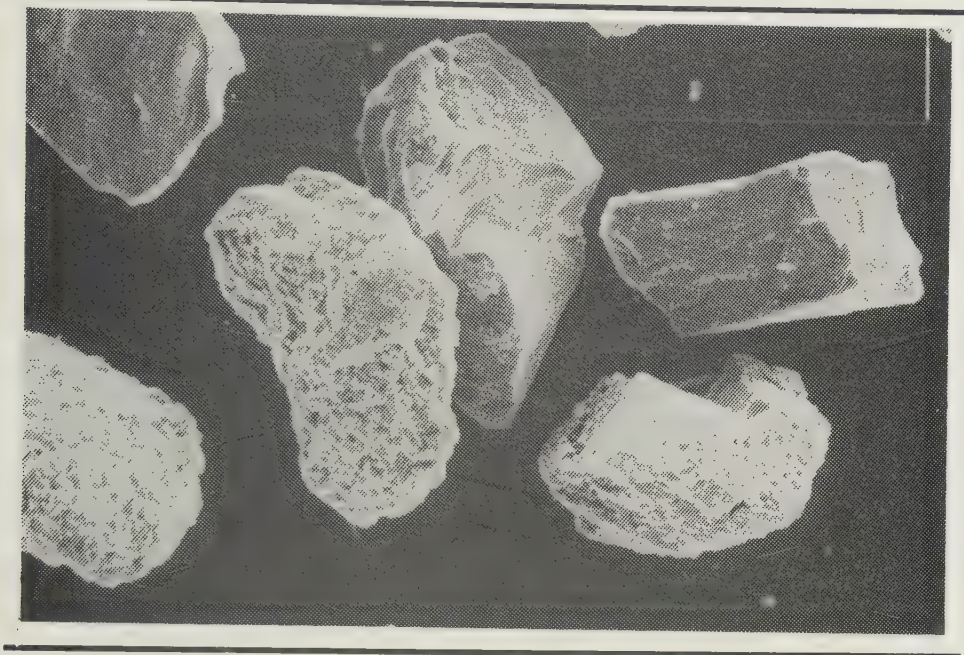


Fig. 3 and 4. *These are photographs as Fig. 1 and 2, but made of a fraction obtained as 90—100 microns after wet sieving. They are of relatively equal size and have an average size of about 90—100 microns. No smaller particles can be detected.*

It is quite obvious that if the two fractions, the dry method fraction and the wet method fraction, are used in experiments they would give quite different results and conclusions, if they both were to be considered as only 90—100 micron particles.

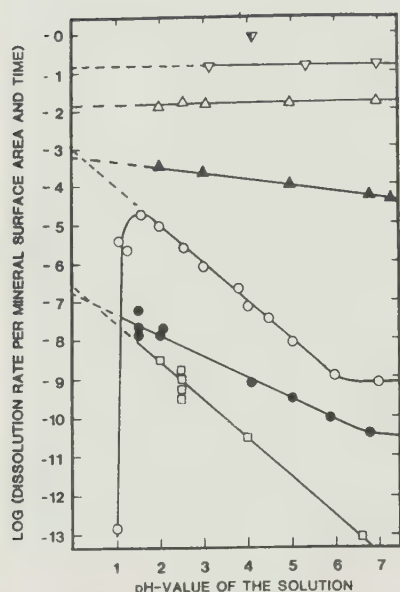


Fig. 5. The diagram shows the dissolution rate per particle surface area as a function of the pH-value of the solution. The dissolution rate is given as $\text{Kmol/m}^2\cdot\text{s}$. The inverted black-and-white triangle (∇) represents sodiumhydroxide, the inverted triangles (∇) represents sodium carbonate, the triangles (Δ) represents the dissolution of slaked lime in hydrochloric acid, the black triangles ($\blacktriangle$) represents the dissolution of slaked lime in sulfuric acid. The open circles ($\circ$) represents the dissolution of calcite, the black dots ($\bullet$) dolomite, and the boxes ($\square$) represents the dissolution of olivine.

The observed mass transfer coefficients can be compared to those predicted by the theory in Fig. 11. The line represents the equation given by Sherwood et al (1):

$$K_M = \frac{D^0}{D_p} (2 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3}) \quad (26)$$

The way the dissolution rate per surface area depends on the hydrogen ion is shown in Fig. 5 for olivine, dolomite, calcite and slaked lime. The dissolution of calcite and olivine is proportional to the hydrogen ion concentration at lower pH values than pH 6.5. At sulfate concentration above 10^{-2} m the calcite surface gets saturated with

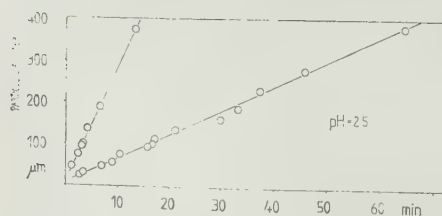
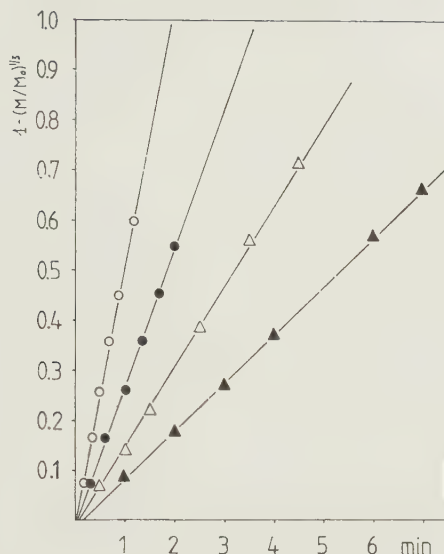


Fig. 6. The time for 50 % dissolution and the time for 100 % dissolution is plotted versus particle diameter for some of the particle sizes used in the experiments. The theory predict that they should be located along the straight lines. This diagram applies for $\text{pH}=2.5$.

Fig. 7. The kinetics of dissolution for some of the particle fractions used in the experiments. $1-(M/M_0)^{1/3}$ versus time is plotted here. The open circles represent the fraction 11—15 microns, the black dots 15—23 microns, the open triangles 23—33 microns and the black triangles 33—43 microns.



precipitated gypsum, and as a result the dissolution rate rapidly falls to zero below pH 2.0 in sulfuric acid. The dissolution of calcite is clearly controlled by diffusion of the hydrogen ion between pH 2.0 and pH 6.5 and can be illustrated with equation (15) and its limiting cases. Above pH 6.5 the dissolution changes mechanism.

Table 1. The measured mass transfer coefficients for different particle sizes. C is the correlation between the experimental points and the straight line represents the theory. K_M is the mass transfer coefficient measured. The very small particles did not give the same accuracy due to their having been produced by sedimentation in very small amounts. The values of K_M is therefore approximate and may vary $\pm 40\%$.

Particle size	Correlation	Mass transfer coefficient
11.2—14.9 μm	0.9990	$(1.04 \pm 0.16) \cdot 10^{-3} \text{ ms}^{-1}$
14.9—22.7 μm	0.9992	$(0.75 \pm 0.16) \cdot 10^{-3} \text{ ms}^{-1}$
22.7—32.5 μm	0.9995	$(0.65 \pm 0.12) \cdot 10^{-3} \text{ ms}^{-1}$
32.5—43.1 μm	0.9996	$(0.55 \pm 0.08) \cdot 10^{-3} \text{ ms}^{-1}$
18—25 μm	0.98	$(0.76 \pm 0.12) \cdot 10^{-3} \text{ ms}^{-1}$
25—30 μm	0.994	$(0.93 \pm 0.09) \cdot 10^{-3} \text{ ms}^{-1}$
46—50 μm	0.9996	$(0.94 \pm 0.04) \cdot 10^{-3} \text{ ms}^{-1}$
64—90 μm	0.998	$(1.00 \pm 0.17) \cdot 10^{-3} \text{ ms}^{-1}$
90—100 μm	0.995	$(0.87 \pm 0.05) \cdot 10^{-3} \text{ ms}^{-1}$
100—104 μm	0.9996	$(0.84 \pm 0.02) \cdot 10^{-3} \text{ ms}^{-1}$
100—125 μm	0.9995	$(0.91 \pm 0.10) \cdot 10^{-3} \text{ ms}^{-1}$
125—147 μm	0.9992	$(0.81 \pm 0.08) \cdot 10^{-3} \text{ ms}^{-1}$
177—200 μm	0.9992	$(0.79 \pm 0.05) \cdot 10^{-3} \text{ ms}^{-1}$
354—400 μm	0.9995	$(0.81 \pm 0.05) \cdot 10^{-3} \text{ ms}^{-1}$
0.15—0.25 μm		0.09 ms^{-1}
0.11—0.15 μm		0.08 ms^{-1}
0.40—0.60 μm		0.029 ms^{-1}
0.90—1.1 μm		0.009 ms^{-1}

Table 2. The mass transfer coefficient as function of pH-value for dissolution of calcite.

K _M	pH
1.00	0.0
1.13	$(1.0 \pm 0.05) \cdot 10^{-4} \text{ ms}^{-1}$
1.35	$(7.3 \pm 0.38) \cdot 10^{-5} \text{ ms}^{-1}$
1.50	$(0.8 \pm 0.04) \cdot 10^{-3} \text{ ms}^{-1}$
2.00	$(0.87 \pm 0.05) \cdot 10^{-3} \text{ ms}^{-1}$
2.50	$(1.26 \pm 0.07) \cdot 10^{-3} \text{ ms}^{-1}$
3.00	$(1.11 \pm 0.06) \cdot 10^{-3} \text{ ms}^{-1}$
3.80	$(1.66 \pm 0.08) \cdot 10^{-3} \text{ ms}^{-1}$
4.00	$(0.84 \pm 0.04) \cdot 10^{-3} \text{ ms}^{-1}$
4.30	$(1.27 \pm 0.07) \cdot 10^{-3} \text{ ms}^{-1}$
4.50	$(1.34 \pm 0.07) \cdot 10^{-3} \text{ ms}^{-1}$
5.00	$(0.88 \pm 0.05) \cdot 10^{-3} \text{ ms}^{-1}$
6.00	$(1.37 \pm 0.07) \cdot 10^{-3} \text{ ms}^{-1}$
7.00	$(4.0 \pm 0.21) \cdot 10^{-3} \text{ ms}^{-1}$

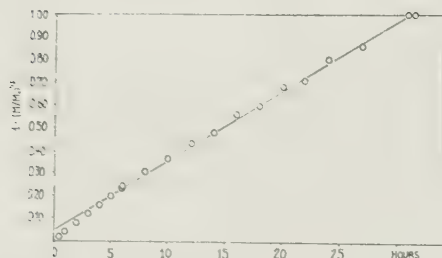


Fig. 8. $1 - (M/M_0)^{1/3}$ is plotted versus time for dolomite at pH 2.5 for the fraction 90–100 microns.

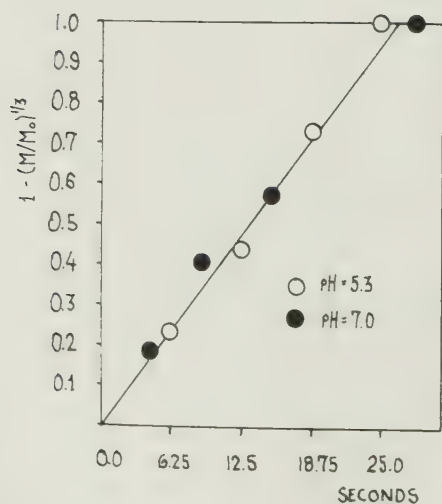
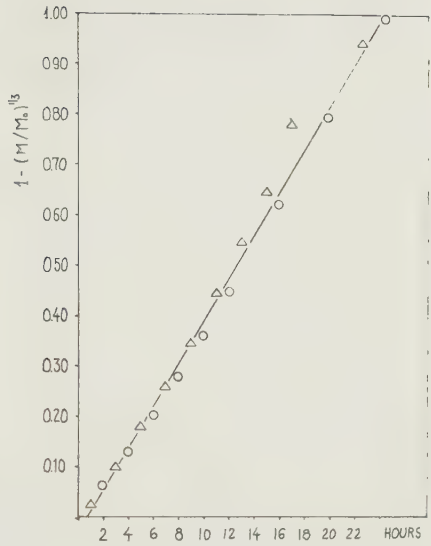
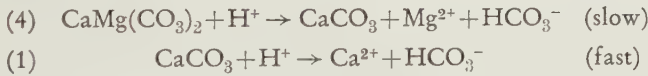


Fig. 9. $1 - (M/M_0)^{1/3}$ is plotted versus time for sodium carbonate. In this case as for slaked lime the dissolution is independent of pH.

Fig. 10. $1 - (M/M_0)^{1/3}$ is plotted versus time for calcite in water containing 1.8 mg/l Fe^{3+} and 1.5 mg/l Al^{3+} as compared to pure water. The triangles represent the line for pure water. For falling or sinking particles the hydrodynamic conditions are such that content of iron and aluminium less than 100 mg/l does not influence the dissolution process substantially. The experiment were conducted with water with a pH-value equal to 4.5.



The dissolution of olivine and dolomite is chemically controlled. The dissolution rate is unaffected by the stirring speed as long as the particles are kept suspended in the liquid. This is in agreement with data elsewhere (4). The dependency on the square root of the hydrogen ion concentration arises from the chemical reaction stoichiometry part that controls the process.



The limiting step becomes:

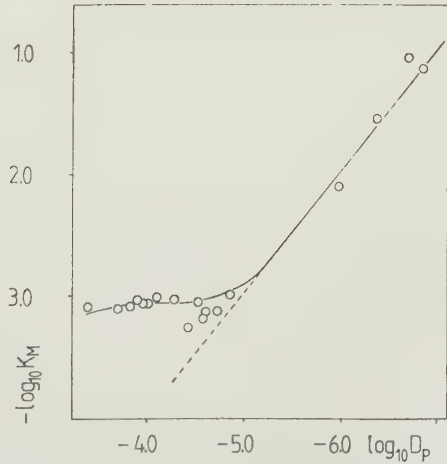
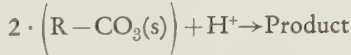


Fig. 11. The observed mass transfer coefficients are here plotted versus particle diameter. The values predicted by equation (26) are indicated by the drawn line.

Table 3. The table gives the limiting values for the dissolution rate constants obtained from fig. 5 according to equation (24) and (25). n is the slope of the dissolution curve and determines the power of the dependency upon the hydrogenion concentration of the dissolution.

Dissolution in H ₂ SO ₄			
	K		n
Calcite	1.36 · 10 ⁻³	m/s	1.00
Dolomite	1.4 · 10 ⁻⁶	$\left(\frac{\text{Kmol}}{\text{m}^3}\right)^{1/2} \cdot \frac{\text{m}}{\text{s}}$	0.509
Olivine	4.1 · 10 ⁻⁷	m/s	1.00
Slaked lime . . .	5.0 · 10 ⁻⁴	$\left(\frac{\text{Kmol}}{\text{m}^3}\right)^{3/4} \cdot \frac{\text{m}}{\text{s}}$	0.246
Soda	0.11	$\left(\frac{\text{Kmol}}{\text{m}^2\text{s}}\right)$	0.00
Dissolution in HCl			
Slaked lime . . .	1.3 · 10 ⁻²	$\frac{\text{Kmol}}{\text{m}^2\text{s}}$	0.00

or rephrased:



and the kinetic expression:

$$r = K_R \cdot [\text{H}^+]^{1/2} \tag{27}$$

The values of the different masstransfer coefficients and chemical reaction rate constants can be taken from Fig. 5 with the relation given by eq. (25) and they are listed in Table 3.

The dissolution of soda and slaked lime

Slaked lime and soda are occasionally used in lake liming and we will treat them here too.

The dissolution of these minerals from the solid is very rapid and more or less independent of pH.

The dissolution is dependent on the diffusion of soda or slaked lime from the surface to the bulk of the liquid. The difference of dissolution rate is related to the relation:

$$\frac{r_{\text{Na}_2\text{CO}_3}}{r_{\text{Ca}(\text{OH})_2}} = \frac{D^{\circ}_{\text{CO}_3^{2+}} \cdot \overset{\text{surface}}{C_{\text{CO}_3^{2+}}}}{D^{\circ}_{\text{OH}^-} \cdot \overset{\text{surface}}{C_{\text{OH}^-}}} \tag{28}$$

The relation predicts that the quotient should be 38.4 and the actual observed value was 40.0. This value would of cause be subject to variations with temperature, the way the solubilities are, as the concentrations in equation (28) are the saturation concentrations at the solid particle surface of the diffusing species.

The effect of CO₂

Plummer et al. (3) treats the problem connected with the effects of dissolved CO₂. He has shown that the general expression for the dissolution at any pH and CO₂-concentration can be expressed as:

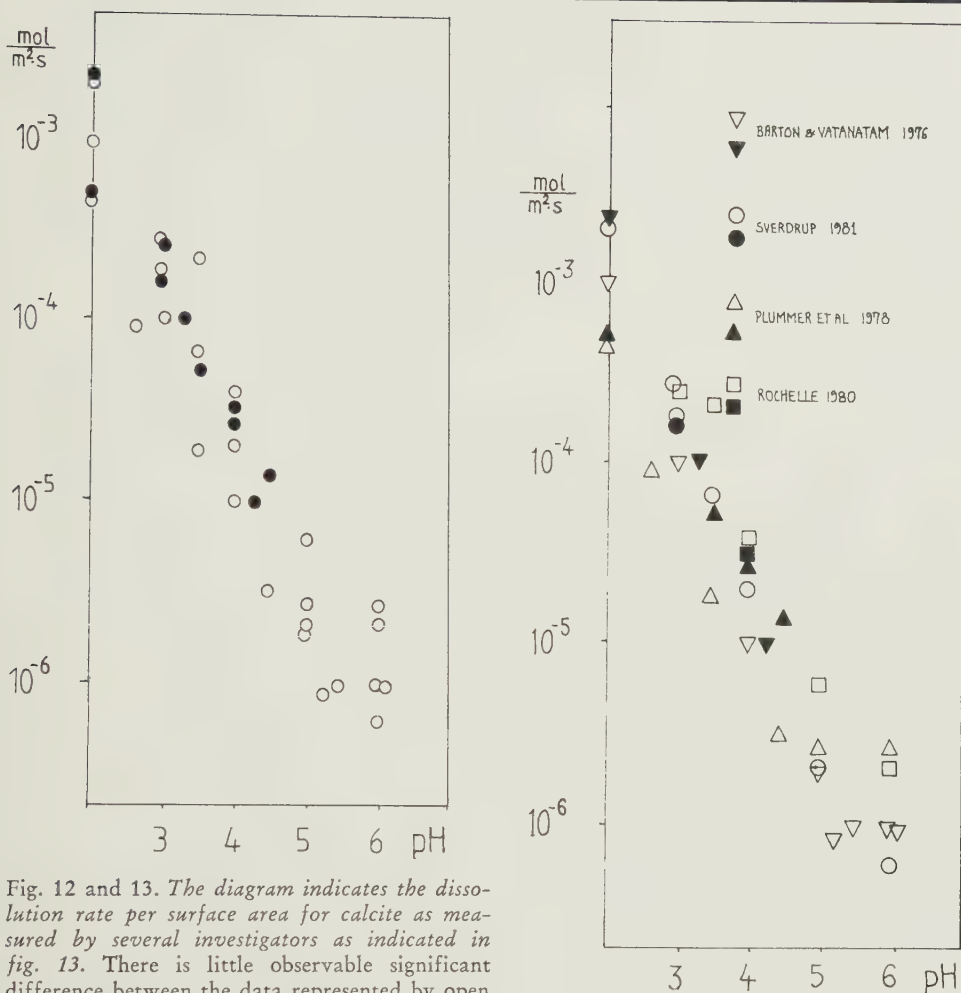


Fig. 12 and 13. The diagram indicates the dissolution rate per surface area for calcite as measured by several investigators as indicated in fig. 13. There is little observable significant difference between the data represented by open circles, which were systems open to air and those marked with black dots which were under a partial CO_2 pressure equal to one atm.

$$\left(\frac{\partial^2 M}{\partial A \partial t} \right) = r = K_1 a_{\text{H}^+} + K_2 a_{\text{CO}_2} + K_3 a_{\text{H}_2\text{O}} - K_4 a_{\text{Ca}^{2+}} \cdot a_{\text{HCO}_3^-} \quad (29)$$

For waters in equilibrium with air, the rate is solely dependent on the hydrogen ion concentration at pH values below 6.5.

For systems open to air or in equilibrium with air, there are several data available. There are data for systems with partial pressure of CO_2 equal to 1.0 atm as well, and these are all given in Fig. 12. It can be seen that as for the dissolution of suspended calcite particles, the partial pressure of CO_2 have little effect at pH-values below 6.0. The data taken from (3), (5), (7), (8) and the author. It can also be seen that the dissolution rate depends linearly upon the hydrogen ion for systems open to air below a pH value of 6.5.

Sammanfattning

Innan man kallar sura sjöar i Sverige, är det av stor vikt för utvecklingen av metoderna att man har kunskap om de processer som styr upplösningen.

Vi önskar här redogöra för den kunskap som finns idag på detta område. Det kan konstateras att upplösningshastigheten för kalksten är nästan uteslutande beroende på två parametrar: kornstorleken och pH-värdet i vattnet. Vidare kan man fastslå att dolomit och olivin är mindre lämpliga än kalksten. Man kan ställa upp ekvationer som väl beskriver det verkliga förloppet och som kan tjäna som utgångspunkt i upplösningsberäkningar.

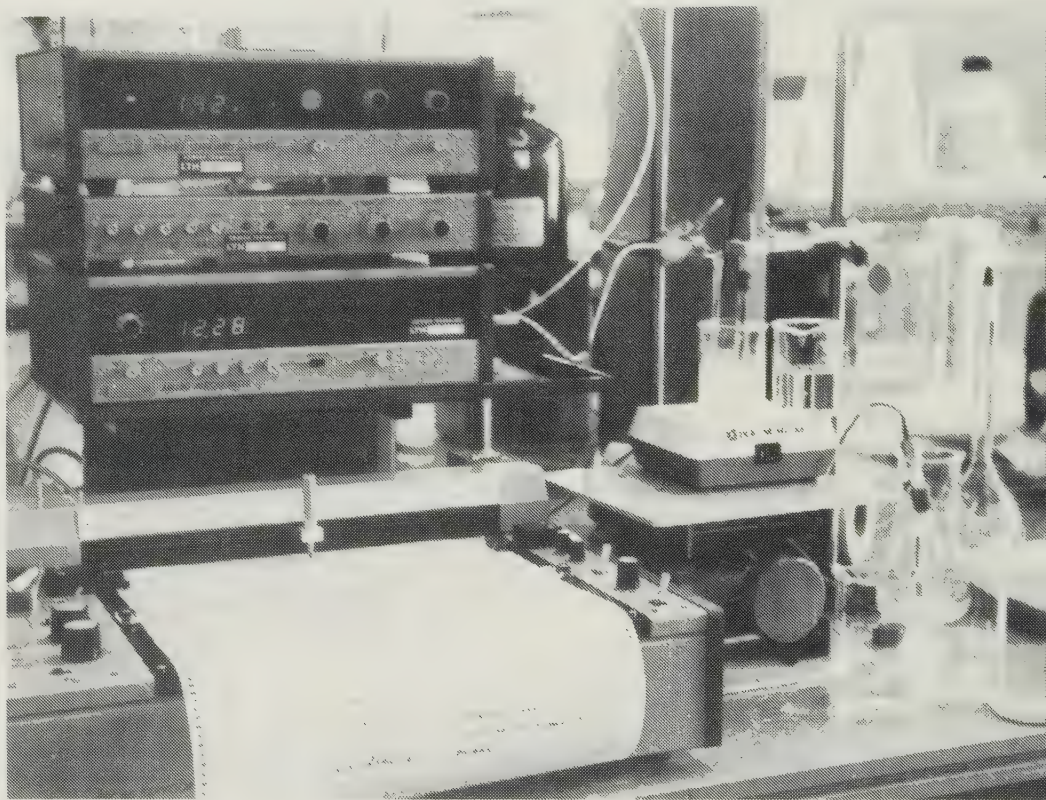
List of Symbols

a_i	Activity of species i
A	Particle surface area varying with time
C	Concentration
C_R	Concentration at the particle surface
C_L	Bulk concentration in the liquid
C_K	Concentration of solid in the particle
ΔC	Concentration difference
D	Diffusivity
K_M	Mass transfer coefficient
K_R	Chemical reaction rate constant
K	Rate constant
M	Mass
M_0	Initial mass
M_E	Conversion factor from moles to kg
n, m	Order of reaction
R	Radius
R_0	Initial radius
R_p	Particle radius
ΔR	Thickness of boundary layer
r	Dissolution rate per surface area
Re	Reynolds number
Sc	Schmidt number
t	Time
ρ_p	Particle density

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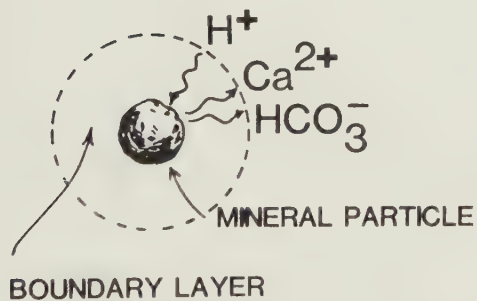
The pH-stat is a very valuable tool for determining the dissolution kinetics of a solid dissolving in acidic water. The apparatus consists of an autoburette, a pH-meter, an autotitrator and a chart recorder.

The pH-stat is designed to keep the pH-value in a reaction vessel constant during experiments. When reactions consuming hydrogen ions are studied, the pH-value of the solution is continuously monitored and any change compensated for by a controlled addition of acid. The amount acid consumed is recorded as a function of time on the chart recorder.

A GENERAL METHOD FOR DETERMINING THE
DISSOLUTION KINETICS OF A MINERAL IN
AQUEOUS SOLUTION, APPLIED TO K-SLAG,
A TRICALCIUMSILICATE.

by

Harald Sverdrup, Per Warfvinge and
Ingemar Bjerle



Submitted for publication to the Geo-
chimica et Cosmochimica Acta, 1985.

ABSTRACT

Based on experimental studies in a pH-stat the dissolution kinetics for K-slag, a tricalcium silicate, was determined. The general expression is:

$$-\frac{dm}{dt} = (K_1 \cdot [H^+]^{2/3} + K_W - K_B \cdot [SiO_2]^{1/3}) \cdot \frac{3 \cdot m}{c \cdot r} \quad (Kmol/s)$$

where the rate constants at 20°C are given by: $pK = 5.06 \pm 0.18$, $pK_W = 7.85 \pm 0.08$ and $pK_B = 7.0 \pm 0.6$. The dissolution of K-slag is slower than calcite dissolution but faster than dolomite dissolution at pH-values below pH 5. At pH-values above pH 6 the dissolution rate is slightly faster than calcite.

The study demonstrates a general determining procedure for the dissolution kinetics of solid mineral particles in aqueous solution.

Introduction

In Sweden, acidification of the environment through deposition of acidic substances, has become a major problem. For affected lakes and streams, neutralization with calcite or other neutralizing agents, is the only large scale countermeasure available, until the emissions of acidifying substances have been reduced.

Calcite is, for many reasons, the mostly used neutralization agent, usually the most cost efficient as well. However locally available K-slag and similar substances may be competitive.

It is necessary to know the exact reaction kinetics in order to be able to plan neutralization operations. In this work we will present a general procedure for determining the dissolution reaction kinetics in aqueous solution and we intend to investigate the dissolution kinetics of K-slag in aqueous solutions, in order to provide such information that it may be compared to other neutralizing agents.

K-slag is a byproduct from the ferrosilicium smelting industry. It is a heterogeneous material consisting mainly of calcium trisilicate but contain other silicates as well:

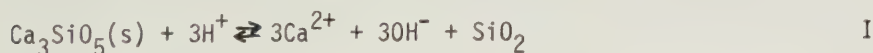
Calciumtrisilicate	Ca_3SiO_5	60-90 %
Calciumdisilicate	Ca_2SiO_4	5-30 %
Calciumsilicate	CaSiO_3	3- 8 %
Calciumoxide	CaO	2- 3 %

K-slag is available from smelter operations and has been used as a neutralizing agent.

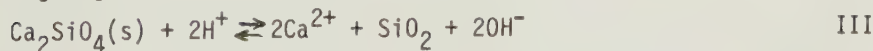
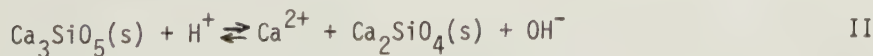
The substance used was K-slag from a smelter operation in Oxelösund, Sweden, delivered by Merox AB. The product called T-slag, produced by a smelter operation in Trollhättan, Sweden, is virtually the same substance.

Chemical reactions in acidic solution

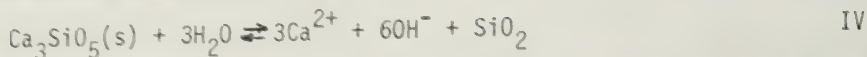
K-slag may react with an acidic aqueous solution in several ways. It may react with the hydrogen ion by congruent dissolution:



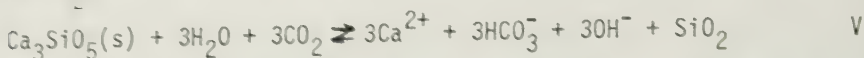
or by incongruent dissolution



The mineral may react with water



If carbon dioxide is present in substantial amounts, or more than a partial pressure of 0.3 atm, K-slag may also include the reaction with CO_2 :



However, the concentration of CO_2 in lake water, streams or in the upper part of the soil, is generally so low (Bouten et al 1984) that the contribution of reaction to the overall reaction rate will be very small.

All of the above reactions are reversible and accordingly the overall reaction rate will always be the sum of the forward reaction rates and the backward reaction rates.

The dissolution reaction starts very far from equilibrium and will by definition try to approach it. The equilibrium concentration is reached at approximately pH 11 in a free drift experiment.

Theory of liquid-solid reaction kinetics

Consider a solid particle dissolving in a liquid. In the dissolution process, several mechanisms occur in series. First the substances that will react with the particle are transported from the bulk of the liquid down to the particle surface. On the surface they will react with the particle in some sort of chemical reaction. Finally the products of the reaction will be transported back into the bulk of the liquid. Generally the mechanism of transport between the solid particle surface and the bulk of the liquid will be molecular diffusion.

When a process takes place as a series of steps, all occurring at different rates, the overall rate of progress for the process will be determined by the slowest step in the series.

If the rate of the chemical reaction is slower than the transport of reactants to the surface by diffusion, the overall reaction rate may be said to be kinetically controlled. If diffusion is the slower process, it is said to be diffusion controlled.

The dissolution of calcite, as an example, is known to be diffusion controlled with respect to hydrogen ion at pH-values lower than pH 5.5, and kinetically controlled with respect to the water reaction at pH-values above pH 6.0. (Plummer et al 1979, Sverdrup & Bjerle 1982.)

If it is assumed that the dissolution of K-slag is proportional to the surface area of each particle and that the dissolution proceeds with w different chemical reactions in the forward direction, and v reactions in the backward direction, the following expression is pertinent:

$$(1) \quad -\frac{dm}{dt} = \left(\sum_{j=1}^W K_j \cdot [C_j]^{n_j} - \sum_{i=1}^V K_{B_i} \cdot [p_i]^{z_i} \right) \cdot \frac{3 \cdot m}{\rho \cdot r} \quad (\text{Kmol/s})$$

In the expression K_j is the forward reaction rate for reactant C_j with the solid at reaction order n_j , and K_{B_i} ; the backward rate for reaction products p_i of reaction order z_i .

We have assumed a mass m of particles, all of the same size r , and the mineral surface area per mass unit of mineral will be given by:

$$(2) \quad A = \frac{3 \cdot m}{\rho \cdot r} \quad (\text{m}^2)$$

where ρ is the density of the particles.

For K-slag we would suggest an expression such as

$$(3) \quad -\frac{dm}{dt} = (K_1 \cdot [H^+]^n + K_W - K_B [SiO_2]^z) \cdot \frac{3 \cdot m}{\rho \cdot r} \quad (\text{Kmol/s})$$

where K_1 is the reaction rate for the reaction with the hydrogen ion, and n the reaction order. K_W is the rate of reaction for water with the mineral, and K_B the backward reaction rate, and the order of reaction is z .

If it is assumed that the K-slag consists mainly of the trisilicate, and reacts with the hydrogen ion congruently according to reaction I, we might expect the order of reaction with respect to the hydrogen ion to be $n = 3$.

However if the trisilicate dissolves incongruently according to reaction II and III, then the order of reaction will be dependent on the amount of moles of reactant consumed per mole of solid dissolved. If reaction II is the rate limiting step, then the dissolution rate will depend on one third of the amount of reactant consumed per mole solid, and we would get $n = 1/3$. However if reaction III is the rate limiting step we should expect $n = 2/3$ (Busenberger et al 1982).

Experience from dissolution of other minerals (Sverdrup & Bjerle 1982), shows that the reaction with the hydrogen ion is dominating at lower pH-values in the solution. For the dissolution of calcite this reaction is diffusion controlled. It is a possibility that such is the case with K-slag as well. Assuming that the reaction with the hydrogen ion is diffusion controlled and the other reactions kinetically controlled, we could write the expression for the dissolution of K-slag as:

$$(4) \quad -\frac{dm}{dt} = \left(D \cdot \left(\frac{\partial [H^+]}{\partial r} \right)_s + K_W - K_B \cdot [SiO_2]^z \right) \cdot \frac{3 \cdot m}{\rho \cdot r} \quad (\text{Kmol/s})$$

where $\left(\frac{\partial [H^+]}{\partial r} \right)_s$ is the gradient of the hydrogen ion concentration at the particle surface. The gradient around a spherical particle is given by the classical equation for diffusion, expressed in spherical coordinates:

$$(5) \quad \frac{\partial [H^+]}{\partial t} = D \cdot \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \cdot (r^2 \cdot (\frac{\partial [H^+]}{\partial r})) \quad (\text{kmol/m}^4)$$

By assuming pseudo-steady-state in the boundary layer, using the conditions in the bulk of the liquid and at the particle surface as boundary conditions, the equation may be solved with respect to the gradient desired (Sverdrup & Bjerle, 1982):

$$(6) \quad D \left(\frac{\partial [H^+]}{\partial r} \right) = D \cdot \left(\frac{1}{\Delta r} + \frac{1}{r} \right) \cdot [H^+] \quad (\text{Kmol/m}^2 \cdot \text{s})$$

As the chemical reaction rate on the surface is much faster than the diffusion rate, the hydrogen ion concentration is here set to zero as compared to the concentration in the bulk of the liquid.

Δr is the boundary layer around the particle through which the diffusion takes place.

In stirred systems we get for particles larger than approximately 10 microns:

$$(7) \quad D \cdot \left(\frac{1}{\Delta r} + \frac{1}{r} \right) \longrightarrow D/\Delta r \quad (\text{m/s})$$

The boundary layer thickness may be calculated with semiempirical relations as given by Sherwood et al (1975).

For particles less than 10 microns and for all stagnant systems regardless of particle size, the expression will become:

$$(8) \quad D \left(\frac{1}{\Delta r} + \frac{1}{r} \right) \longrightarrow D/r \quad (\text{m/s})$$

as $\Delta r \gg r$ in stagnant systems.

For the dissolution of K-slag particles we then get the general expression:

$$(9) \quad - \frac{dm}{dt} = (D \cdot \left(\frac{1}{\Delta r} + \frac{1}{r} \right) \cdot [H^+] + K_W - K_B \cdot [SiO_2]^2) \cdot \frac{3 \cdot m}{\rho \cdot r} \quad (\text{kmol/s})$$

It can be seen that if the dissolution of K-slag is diffusion controlled with respect to the hydrogen ion, then the reaction order of this reaction must be one, $n = 1.0$. As the reaction order of a kinetically controlled reaction may be any number, does this offer a possibility to experimentally determine if the dissolution of K-slag is entirely kinetically controlled.

If the reaction order is found to be $n = 1.0$ then it would be possible to distinguish diffusion control from kinetic control by studying the dissolution of particles smaller than 10 microns. If the reaction is diffusion controlled, it will be proportional to the inverse of the particle size squared, but only proportional to the inverse of the size if the reaction is kinetically controlled.

Experimental

An apparatus called a pH-stat was used to study the dissolution kinetics of K-slag. It consists of a pH-meter, an autotitrator and an autoburette and it is used to keep the pH-value in a reaction vessel constant, by adding acid in the case of dissolution experiments.

For the experiments several particle size fractions of K-slag were prepared by wet sieving. It is of major importance that the particle size fractions are produced in this way, as dry screening will introduce large experimental errors (Sverdrup & Bjerle 1982).

For the experiments fractions with average radii of 17 μm , 22 μm , 27 μm , 33 μm , 40 μm and 70 μm were prepared. Experiments were run at pH 2, pH 2.5, pH 3, pH 3.5, pH 4, pH 5, pH 6.5, pH 7, pH 7.5 and pH 8.5 in dilute sulfuric acidic solution at 25°C.

The pH-stat will as it replaces all hydrogen ions consumed, continuously record the amount of mineral dissolved. Accordingly no analyses of ion concentrations are necessary to determine the dissolution kinetics.

The amounts of mineral dissolved were so small that the activity coefficients for all species involved could be assumed to be constant. The maximum mineral concentration was $2 \cdot 10^{-3} \text{ kmol/m}^3$.

The experimental procedure was identical to the one described by Sverdrup & Bjerle (1981).

An example of an experimental dissolution curve is shown in figure 1.

Interpretation of the results

The experiments showed that the dissolution of K-slag is pH-dependent at pH-values below pH 5. To determine the order of reaction for the reaction of the hydrogen ion with K-slag we may use a part of equation (3):

$$(10) \quad -\frac{dm}{dt} = K_1 \cdot [\text{H}^+]^n \cdot \frac{3 \cdot m}{\rho \cdot r} \quad (\text{Kmol/s})$$

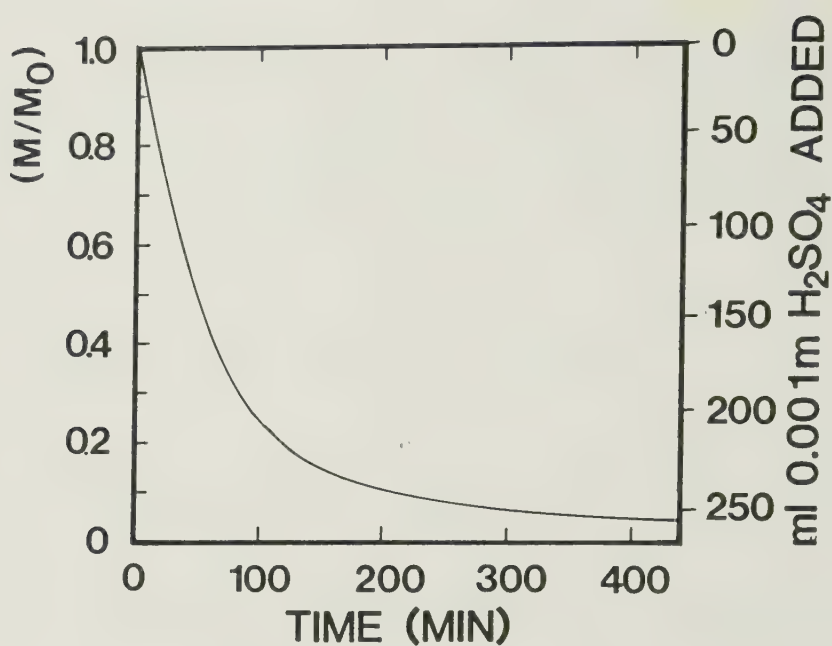


Figure 1 a

Exampel of data from a dissolution run with the pH-stat. The experi-
ment was carried out with K-slag with an initial radius of $17\mu m$, at
pH 7.0.

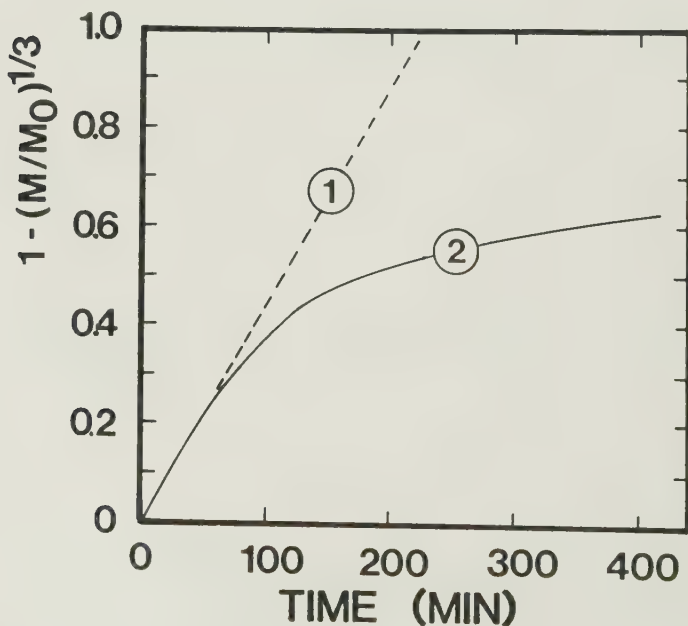


Figure 1 b

In order to determine the backward reaction, the data are reinter-
preted and $1 - (m/m_0)^{1/3}$ is plotted versus the time. The line marked
1 represents expression (17), and 2 expression (18).

By transforming the variables, introducing the dissolved fraction:

$$(11) \quad X = 1 - (m/m_0) \quad (\%/100)$$

we get:

$$(12) \quad - \frac{dX}{dt} = K_1 \cdot [H^+]^n \frac{3 \cdot (1-X)}{2 \cdot r} \quad (s^{-1})$$

By rearranging and taking the logarithm of each side we get the expression

$$(13) \quad \log \left(\frac{dX}{dt} \frac{P \cdot r}{3 \cdot (1-X)} \right) = n \cdot pH + \log K_1$$

At the start of the experiment r will be equal to the initial radius and x will be equal to zero. By plotting the expression on the left at initial conditions versus the pH-value for experiments at different pH-values, we will get a line with the slope n and the intercept $\log K_1$ at pH 0. The values obtained in each experiment are shown in table 1. In figure 2 the left side of eq 13 is plotted versus the pH-value of the solution. It can be seen that we get a straight line from pH 2 to pH 5 with a slope of approximately 2/3.

From this we may make the following conclusion.

- The reaction of K-slag with the hydrogen ion in acidic aqueous solution is kinetically controlled.

From the intercept in figure 1 we may determine the actual rate constant:

$$- \log K_1 = 5.06 \pm 0.18$$

and the reaction order

$$n = 0.65 \pm 0.05$$

The statistical correlation of the experimental values to the straight line is fairly good; $r^2 = 0.996$.

It may be seen that the reaction rate is not dependent on the pH-value above pH 5. In this pH-region the reaction with water dominates. As the reaction takes place in aqueous solution, the rate will be virtually of zero order with respect to water. The intercept of the flat part of the curve indicates the constant reaction rate for the water reaction:

$$- \log K_W = 7.85 \pm 0.08$$

r_o	pH	$(\frac{dx}{dt})$	$\log (\frac{dx}{dt} \cdot \frac{\rho \cdot r_o}{(1-x_o) \cdot 3})$
17 μm	2	$6.67 \cdot 10^{-3}$	-3.99
33 μm	2	$3.62 \cdot 10^{-3}$	-4.02
17 μm	2.5	$3.19 \cdot 10^{-3}$	-4.31
22 μm	2.5	$2.14 \cdot 10^{-3}$	-4.35
27 μm	2.5	$1.87 \cdot 10^{-3}$	-4.39
70 μm	2.5	$0.93 \cdot 10^{-3}$	-4.25
17 μm	3	$1.6 \cdot 10^{-3}$	-4.61
17 μm	3.5	$0.86 \cdot 10^{-3}$	-5.04
17 μm	4	$3.18 \cdot 10^{-4}$	-5.31
24 μm	4	$2.66 \cdot 10^{-4}$	-5.24
40 μm	4	$2.61 \cdot 10^{-4}$	-5.03
17 μm	5	$2.17 \cdot 10^{-4}$	-5.48
17 μm	5.8	$2.24 \cdot 10^{-4}$	-5.46
17 μm	6.5	$2.15 \cdot 10^{-4}$	-5.48
17 μm	7.0	$1.9 \cdot 10^{-4}$	-5.54
17 μm	7.5	$1.9 \cdot 10^{-4}$	-5.54
17 μm	8.5	$1.95 \cdot 10^{-4}$	-5.52

Table 1

Results from the experiments in the pH-stat. (dx/dt) is the initial dissolution rate in the experiment.

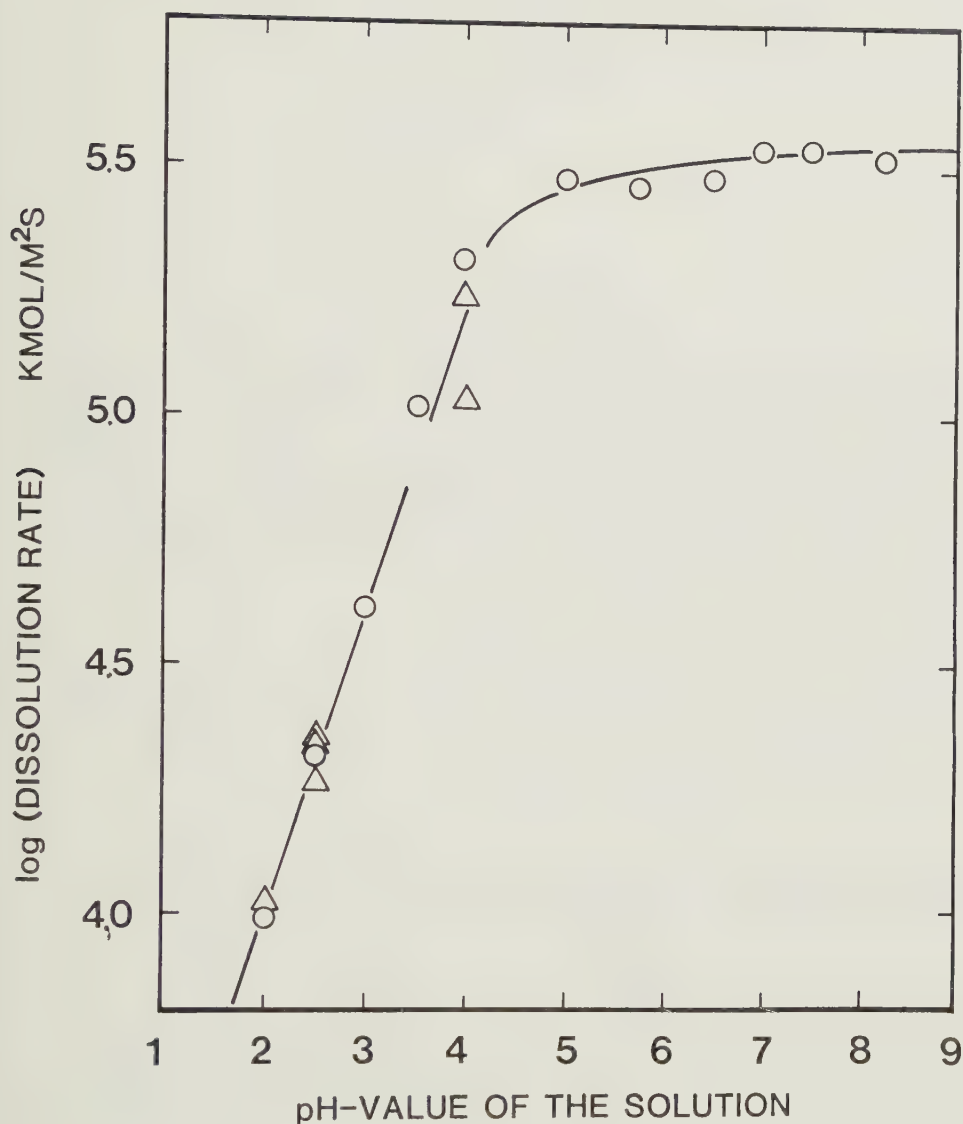


Figure 2

The dissolution rate per mineral surface area as a function of pH-value in the aqueous solution. The slope of the curve is indicating the reaction order with respect to the hydrogen ion, and is equal to $2/3$. The horizontal section indicates where the reaction with water is the dominant mechanism. The circles represent experiments carried out with particles of radius $17\mu\text{m}$. The triangles represent other particle sizes.

The backward reaction rate

We can conclude that eq 2 describes the dissolution of K-slag. If this equation is intergrated using the substitution:

$$(14) \quad r = r_0 \cdot \left(\frac{m}{m_0} \right)^{1/3}$$

the solution becomes

$$(15) \quad 1 - (m/m_0)^{1/3} = (K_1 \cdot [H^+]^{2/3} + KW - KB \cdot [SiO_2]^Z) \cdot \frac{t}{\rho \cdot r_0}$$

In a drawing of $1 - (m/m_0)^{1/3}$ versus time, t , we should expect a straight line if all concentrations were constant. In the pH-stat controlled experiment, the hydrogen ion concentration will be kept constant, but the silicate concentration will rise as the dissolution proceeds. The curve will accordingly fall below the expected straight line for reaction with no silicate present.

We could determine the slope α in the expression:

$$(16) \quad 1 - (m/m_0)^{1/3} = \alpha \frac{t}{\rho \cdot r_0}$$

at $t = 0$, when the experiment starts. The obtained value of α would be equal to α_0 :

$$(17) \quad \alpha_0 = K_1 \cdot [H^+]^{2/3} + KW$$

At any other point in time, when the silicate concentration is not equal to zero, the slope will be given by α_t :

$$(18) \quad \alpha_t = K_1 \cdot [H^+]^{2/3} + KW - KB [SiO_2]^Z$$

where $[SiO_2]$ is the total silicate concentration at the time t . By subtracting the slope at $t = 0$ and some later time t , we get

$$(19) \quad \alpha_0 - \alpha_t = KB \cdot [SiO_2]^Z$$

or

pH	Z	pKB
2	0.35	-7.54
3	0.47	-6.78
4	0.25	-7.14
5	0.35	-7.14
7.0	0.24	-7.44
7.5	0.505	-6.00

Table 2

The result of the interpretation of the backward reaction rate z is the order of reaction, KB is the reaction rate. z has an average value of $z = 0.36 \pm 0.12$.

Time min	m/m_0 0.1 m CaCl_2	m/m_0 no CaCl_2
0	0	
35	0.247	0.217
85	0.475	0.468
135	0.647	0.632
165	0.771	0.747
195	0.850	0.823
295	0.930	0.517

Table 3

The result from two runs to check if the backward reaction rate is dependent on the calcium ion concentration. There is no indication in the data to suggest such a dependency. The maximum silicate concentration during the experiment was $2 \cdot 10^{-3}$ kmol/m, pH was pH 4.0 and the particle size used was 63-71 microns.

$$(20) \quad \log (\alpha_0 - \alpha_t) = z \cdot \log [\text{SiO}_2] + \log \text{KB}$$

By plotting $\log (\alpha_0 - \alpha_t)$ versus $\log [\text{SiO}_2]$ we get a straight line with the slope z and one intercept $\log \text{KB}$. The result obtained by doing this for runs at different pH-values are shown in table 2. As the concentration of silicate does not extend over a large range, the results are somewhat scattered.

We may confine the order of reaction within the limits

$$0.48 > z > 0.24$$

with the mean value $z = 0.36$. The rate constant for the backward reaction may be estimated as

$$- \log \text{KB} = 7.0 \pm 0.6$$

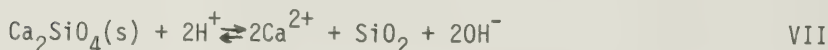
Discussion

It is hard to determine if the backward rate is really dependent on the trisilicate concentration. The concentration used was the total silicate concentration defined as:

$$(21) \quad [\text{SiO}_2] = \frac{m_0 - m}{\text{Vol}}$$

where vol is the volume of solvent. From the data in table 2 we may conclude that the backward rate is independent of the hydroxy ion.

The observed order of reaction may also be explained in the following way. Assume that K-slag dissolves incongruently in two steps:



If the second reaction (VII) is the rate limiting step, then the rate is dependent on 2/3 of the amount of reactants required per mole of solid dissolved. Order of reaction for the process will accordingly be 2/3.

To solve the question of whether the calcium ion has influence on the backward dissolution rate or not a second set of experiments were carried out.

K-slag was dissolved in solutions having different initial concentrations of CaCl_2 .

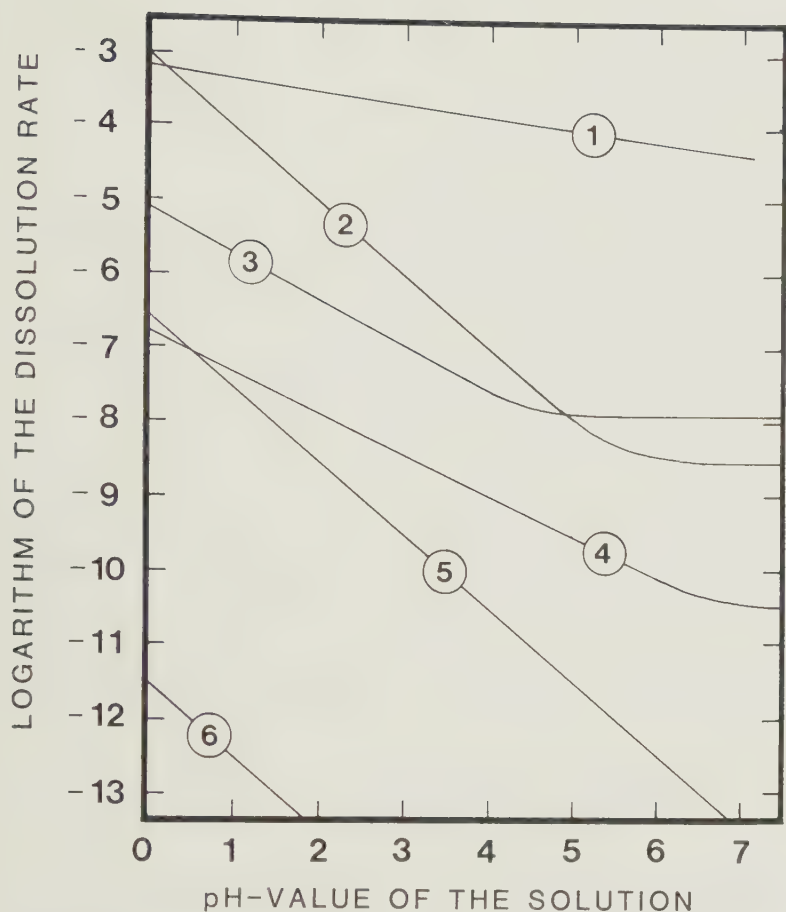


Figure 3

The dissolution rate per mineral surface area as a function of pH for several minerals.

- 1 Slaked lime $\text{Ca}(\text{OH})_2$
- 2 Calcite CaCO_3
- 3 K-slag Ca_3SiO_5
- 4 Dolomite $\text{CaMg}(\text{CO}_3)_2$
- 5 Olivine Mg_2SiO_4
- 6 Feldspar KAlSi_3O_8

An earlier diagram presented in Sverdrup & Bjerle (1982) contained erroneous units which have been corrected in this diagram. The lines reported are based on experimental data from Sverdrup & Bjerle (1982), Busenberger & Clemency (1976), Busenberger & Plummer (1982), Helgeson (1971), Petrovic (1976), and Plummer et al (1979).

If calcium must be incorporated in the backward rate expression, then the expression could be modified to:

$$\alpha_0 - \alpha_t = KB' \cdot [\text{SiO}_2]^Z \cdot [\text{Ca}^{2+}]^Y$$

and the KB measured would be:

$$\log (\alpha_0 - \alpha_t) = Z \cdot \log [\text{SiO}_2] + \log KB$$

$$\log KB = Y \cdot \log [\text{Ca}^{2+}] + \log KB''$$

By plotting the logarithm of the observed KB versus the logarithm of the calcium concentration we would get the reaction order Y as the slope and the logarithm of the rate constant as the intercept.

For the runs made with different initial concentrations of CaCl_2 no difference in backward reaction rate was evident. Hence we may conclude that the backward reaction rate is independent of the calcium ion concentration. The experimental data from two runs are shown in tabel 3.

The general expression for the dissolution of K-slag may be written

$$(22) \quad - \frac{dm}{dt} = (K_1 \cdot [\text{H}^+]^{2/3} + KW - KB \cdot [\text{SiO}_2]^{1/3}) \cdot \frac{3 \cdot m}{\rho \cdot r} \quad (\text{Kmol/s})$$

It is not selfevident that K-slag will dissolve faster in the presence of carbon dioxide in the solution. The overall reaction rate could be expressed as:

$$(23) \quad - \frac{dm}{dt} = (K_1 [\text{H}^+]^{2/3} + KW - KB [\text{SiO}_2]^{1/3} - KC \cdot [\text{Ca}^{2+}] \cdot [\text{HCO}_3^-]) \cdot \frac{3 \cdot m}{\rho \cdot r}$$

where KC is the rate constant for the precipitation of calcite. In the presence of carbondioxide in the solution two backwards reactions will take place, and the total reaction rate would be low.

The dissolution of K-slag in relation to other minerals

In figure 2 we have shown the dissolution rate for several minerals as a function of pH in the solution and included K-slag among them. They are slaked lime, calcite, dolomite, olivine and feldspar.

In table 4 we have listed the pK's of the rate constants where K1 is related to the reaction with the hydrogen ion, K2 to the reaction with carbondioxide, KW to the reaction with water and KB the backward reaction rate. The data were extracted from our own experiments, as well as from the litterature (Sverdrup & Bjerle 1982, Busenberg et al 1982, Helgeson et al 1971).

The order of reaction is listed in tabel 5 for all the minerals considered in table 4.

Mineral	pK_1	pK_2	pKW	pKB
Slaked lime	- 3.3			
Calcite	- 3.0	-6.7	- 8.7	- 2.4
K-slag	- 6.5		- 7.85	- 7.0
Dolomite	- 6.85	-9.3	-10.5	- 7.2
Cement	- 7.0		-7.9	
Olivine	- 6.5		>-13	
Feldspar	-11.5		-16.7	

Table 4

Reaction rate constants for the dissolution of different neutralisation agents. K1 relates to the reaction with the hydrogen ion, K2 to carbondioxide, KW to water and KB to the backward reaction. For the reaction of calcite with the hydrogen ion, generally $K1 = D \cdot (1/r + 1/\Delta r)$ where D is the diffusivity of the hydrogen ion ($D = 10^{-9} \text{ m}^2/\text{s}$).

Mineral	n_1	n_2	n_3	n_4
Slaked lime	1/4			
Calcite	1	1	0	1
K-slag	2/3		0	1/3
Dolomite	1/2	1/2	0	1
Olivine	1		0	
Feldspar	1		0	

Table 5

Order of reaction for the dissolution of different minerals n_1 is with respect to the hydrogen ion, n_2 with respect to carbondioxide, n_3 with respect to water and n_4 to the backward reaction.

LIST OF SYMBOLS

A	Mineral surface area per weight unit	(m ² /kmol)
D	Diffusivity of hydrogen ion	(m ² /s)
C _j	Concentration of reactant j	(kmol/m ³)
H ⁺	Concentration of hydrogen ion	(kmol/m ³)
i	Index	
j	Index	
K _j	Forward rate constant for reaction j	
K _i	Backward rate constant for reaction i	
K ₁	Rate constant for reaction with hydrogen ion	
K	Rate constant for reaction with carbon dioxide	
K _W	Rate constant for reaction with water	
K _B	Backward reaction rate	
m	Mass	(kmol)
m ₀	Initial mass	(kmol)
(dm/dt)	Change in mass with time	(kmol/s)
n	Reaction order of reaction with hydrogen ion	
P _i	Concentration of reaction product i	(kmol/m ³)
r	Radius	(m)
Δr	Thickness of boundary layer	(m)
r ₀	Initial radius	(m)
x	Dissolved fraction	(%/100)
z	Reaction order of backward reaction	
w	Number of forward reactions	
v	Number of backward reactions	
t	Time	(s)
vol	Volume of solution	(m ³)
α ₀	Initial rate of reaction	(kmol/m ² ·s)
α _t	Reaction rate at time t	(kmol/m ² ·s)
ρ	Density of solid mineral	ρ = 2700 kg/m ³

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Lake Liming

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Abstract

Based on knowledge available to us from experiments and literature, it is our intentions in this study to present a theory concerning the dissolution of calcite which is sinking in a lake. The basic equation for the dissolution can be given as:

$$X = \sum_{i=1}^n \Delta\phi_i X_i = \sum_{i=1}^n \frac{\Delta\phi_i}{R_i^2} \cdot A_i \cdot \Delta H^+ \cdot S \cdot \left(1 - \left(1 + \sum_{j=i-1}^{n-1} j \right) B \right. \\ \left. + \left(1 + \sum_{j=i-1}^{n-2} \left(\sum_{j=i-1}^{n-1} j \right) \right) B^2 - \dots + \left(1 + \sum_{j=i-1}^1 \dots \right. \right. \\ \left. \left. \dots \times \sum_{j=i-1}^{n-2} \left(\sum_{j=i-1}^{n-1} j \right) \right) \dots \right) B^n \cdot (-1)^n \Bigg)$$

This equation is based on a diffusion model for the dissolution. This study also presents a model for evaluating different calcite powders offered commercially for liming operations.

List of symbols

A_L	Lake surface area
$A(t)$	Surface area of particle
C	Concentration
C_L^0	Initial concentration in the lake
C_L	Concentration in the lake
C_R	Concentration at the particle surface
D	Diffusivity
D_H^0	Diffusivity of H^+ -ion
g	Gravitational acceleration
K_M	Mass transfer coefficient
M	Mass
M_i	Mass of particle fraction i
M_0	Initial mass
M_E	Neutralization equivalent for calcite
M^*	Amount calcite per lake area, dosage of calcite: M_0/A_L
P	Fraction of the total lake area treated
R	Radius
R_i	Radius of particle i initially
R_0	Initial radius
ΔR	Boundary layer thickness
S	Mean lake depth, sinking depth of particle
t	Time
V	Velocity of sinking particle
V_L	Volume of water treated ($V_L = P \cdot A_L \cdot S$)
X	Dissolved fraction
ρ_P	Density of particle
ρ_V	Density of water
$\Delta\phi_i$	Fraction i from an amount
μ	Viscosity

$A, B, \alpha, \beta, \theta$ are substitution constants for other constants.

Introduction

Thousands of lakes and rivers in Scandinavia and North America located on low weathering bedrock or surrounded by soils with a low calcite content are suffering from the effects of acid rain.

In Norway and Sweden waters in the southern parts of the countries, an area of almost 200 000 km², will have critical pH-values during some time of the year.

Nearly forty thousand lakes are affected, in addition to countless kilometers of rivers and brooks.

The measure most frequently taken is applying calcite in different ways to the river or lake affected. This is in fact the only large scale remedy available until emissions of SO₂ and NO_x have been reduced drastically on the European continent.

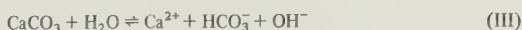
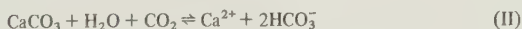
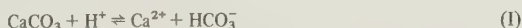
In Sweden large programs for liming of lakes and running waters are in progress and despite the stressed state finances, about 200 million Swedish kronor will be spent each year in the final program. In Southern Sweden the total amount needed for neutralization is estimated to be about 800 000 tons of calcite each year. It is quite obvious that it is of greatest importance to use the resources as efficiently as possible. The desired result of liming of lakes and running waters is that every cubic meter treated achieves a good pH-value and alkalinity. This is achieved by dissolving at least the amount needed for neutralization of the acidic water. The fraction not dissolved is of no interest and is lost or wasted. Accordingly, the total neutralization cost depends not only on calcite cost but on fraction dissolved as well.

The dissolution rate for calcite particles sinking in water is very much larger than when they have precipitated on the lake bottom. This implies that the time required to dissolve any significant amount is so long, that sedimentation along with inhibition by humus will stop the dissolution totally. The rate is in this case too slow to keep up with the need for steady neutralization. There is no great difference between the dissolution rates for calcite on the bottom and soil liming in general. Accordingly, the major part of the calcite ever to be dissolved, dissolves during the time of sinking.

The purpose of our study is to present a theory which will allow us to make predictions, and test our predictions against the observed results from a number of Swedish lake liming projects.

Dissolution of calcite in natural lake water

The dissolution of solid calcite in dilute acid can be described as a heterogeneous solid-liquid reaction. The chemical reactions involved are:



In natural lake waters with a pH-values less than pH 6.5, reaction (I) will dominate, and for pH-values above 6.5, reaction (III) will play an important role. In most cases the lakes considered in this study will contain too little dissolved CO_2 for reaction (II) to be of any importance.

In lake liming we operate in the range from pH 4.0 to pH 6.5 and within this range, reaction (I) dominates. Under these conditions the dissolution rate is linearly dependent on the hydrogen ion concentration, and the process controlled by the diffusion of this ion. It can be described with mass transfer models following the principles outlined by Sherwood *et al.* [1] and Crank [2]. See also [3], [8] and [13].

Theory

The model considers calcite powder sinking in an acidified lake. The larger particles will sink the fastest, and as they dissolve, the water in their wake will be partially neutralized and have a slightly raised pH-value in front of the next particles sinking somewhat slower.

The dissolution will depend on the hydrogen ion gradient around the particle; $(\partial C/\partial R)$, and the basic equations are:

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial R^2} + \frac{2}{R} \frac{\partial C}{\partial R} \right) \quad (1)$$

$$-\frac{\partial M}{\partial t} = D \left(\frac{\partial C}{\partial R} \right)_R \cdot A(t) \cdot M_E \quad (2)$$

with the boundary conditions

$$\begin{aligned} C &= C_R & C &= C_L \\ R &= R & R &= R + \Delta R \end{aligned} \quad (1a)$$

and

$$M = M_0 \quad t = 0 \quad (2a)$$

As acidified lakes and limed lakes lie in the pH-range between pH 4 and pH 6.5, it is assumed that in this range the neutralization will be proportional to the amount of calcite dissolved. This assumption does not introduce large errors which can be deduced from studies such as [8] and [9].

For the neutralization we write:

$$\frac{\partial M}{\partial t} = \left(\frac{\partial C}{\partial t} \right)_L \cdot V_L \cdot M_E \quad (3)$$

with the boundary condition:

$$M = M_0 \quad C = C_0 \quad (3a)$$

Pseudo-steady state is assumed for the dissolution and we get from eqs. (1) and (2) according to the film theory:

$$K_M = \frac{D}{\Delta R}$$

and

$$D \left(\frac{\partial C}{\partial R} \right)_R = K_M (C - C_R) \quad (4)$$

Integration of eq. (3) gives:

$$C = C_L^0 - \left(\frac{M_0 - M}{V_L \cdot M_E} \right) \quad (5)$$

The surface area $A(t)$ can be expressed as

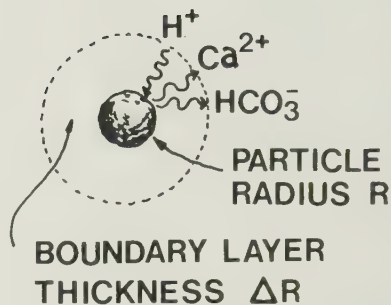


Fig. 1. The boundary layer model.

$$A(t) = \frac{3}{R_0 \cdot \rho_P} \cdot M_0^{1/3} \cdot M^{2/3} \quad (6)$$

and the treated volume V_L as

$$V_L = A_L \cdot P \cdot S \quad (7)$$

Equations (4), (5), (6) and (7) can be inserted in eq. (2) to give an expression for the dissolution of calcite particles.

Particles smaller than $100 \mu\text{m}$ in diameter sink with velocities given by Stokes equation:

$$V = \frac{4R^2 \cdot g(\rho_P - \rho_V)}{18\mu} \quad (8)$$

and the definition of velocity:

$$V = \frac{dS}{dt} \quad (9)$$

The particles are considered as spherical

$$R = R_0 \cdot \left(\frac{M}{M_0} \right)^{1/3} \quad (10)$$

If all the eqs. (4)–(10) are inserted in eq. (2) and dt substituted with dS , we get for the dissolution of all particles of initial radius R_i :

$$-\frac{dM}{dS} = \frac{A \cdot \Delta H^+}{R_i^3} \quad (11)$$

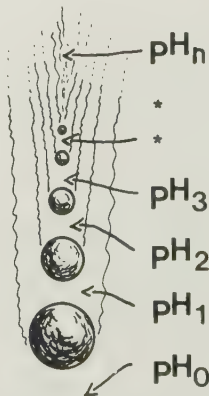


Fig. 2. The sinking-dissolving model. The fastest sinking particle will partially neutralize the water in which it is sinking and raise the pH-value of the water behind it.

where

$$A = \frac{27K_M \cdot M_E \cdot M_0 \cdot \mu}{2\rho_P(\rho_P - \rho_V)g} \quad \text{and} \quad \Delta H^+ = C_L^0 - C_R \quad (12)$$

The largest particle will sink fastest, and leave the water behind it partially neutralized. The particle following in its wake will travel through water with a higher pH-value. Accordingly we get for all the particles in a calcite powder:

$$\begin{aligned} -\frac{dM}{dS} &= \frac{d}{dS} (M_1 + M_2 + \dots + M_n) \\ &= \frac{A(C_1 - C_R)}{R_1^3} \Delta\phi_1 + \dots + \frac{A(C_n - C_R)}{R_n^3} \Delta\phi_n \end{aligned} \quad (13)$$

which can be written as the general equation for the dissolution of a sinking calcite powder:

$$-\frac{d}{dS} \sum_{i=1}^n (M_i) = A \sum_{i=1}^n \left(\frac{\Delta H^+ - \sum_{j=i-1}^{n-1} \left(\frac{M_0 - M_j}{A_L \cdot P \cdot S \cdot M_E} \right)}{R_i^3} \right) \Delta\phi_i \quad (14)$$

In order to rearrange eq. (14) we write:

$$\frac{dX_1}{dS} = \frac{A \cdot \Delta H^+}{R_1^3} \quad (15)$$

$$\frac{dX_2}{dS} = \frac{A}{R_2^3} \left(\Delta H^+ - \frac{B}{S} X_1 \right) \quad (16)$$

$$\vdots$$

$$\frac{dX_n}{dS} = \frac{A}{R_n^3} \left(\Delta H^+ - \frac{B}{S} (X_1 + X_2 + \dots + X_{n-1}) \right) \quad (17)$$

with the dissolved fraction defined as:

$$\begin{aligned} X_i &= 1 - \frac{M_i}{\Delta\phi_i M_0} \\ X &= \sum_{i=1}^n \Delta\phi_i X_i \end{aligned} \quad (18)$$

The solution of eq. (14) can be expressed as

$$\sum_{i=1}^n \Delta\phi_i X_i = A' \cdot \Delta H^+ \cdot S \sum_{i=1}^n \frac{\Delta\phi_i}{R_i^3} (1 - P_i(B)) \quad (19)$$

in which $P_i(B)$ is the polynomial

$$\begin{aligned} P_n(B) &= \left(1 + \sum_{i=0}^{n-1} i \right) B + \left(1 + \sum_{i=0}^{n-2} \left(\sum_{j=0}^{n-1} i \right) \right) B^2 - \dots \\ &\dots + (-1)^n \cdot \left(1 + \sum_{i=0}^{n-1} \dots \sum_{i=0}^{n-2} \left(\sum_{i=0}^{n-1} i \right) \right) \dots B^n \end{aligned} \quad (20)$$

and

$$A' = \frac{A}{M_0}, \quad B = \frac{A' \cdot M^*}{P \cdot M_E}$$

The solution of eq. (14) is:

$$\begin{aligned} X &= A' \cdot \Delta H^+ \cdot S \cdot \sum_{i=1}^n \frac{\Delta\phi_i}{R_i^3} \left(1 - \left(1 + \sum_{j=i-1}^{n-1} j \right) B \right. \\ &\quad \left. + \left(1 + \sum_{j=i-1}^{n-2} \left(\sum_{j=i-1}^{n-1} j \right) \right) B^2 - \dots \right) \end{aligned}$$

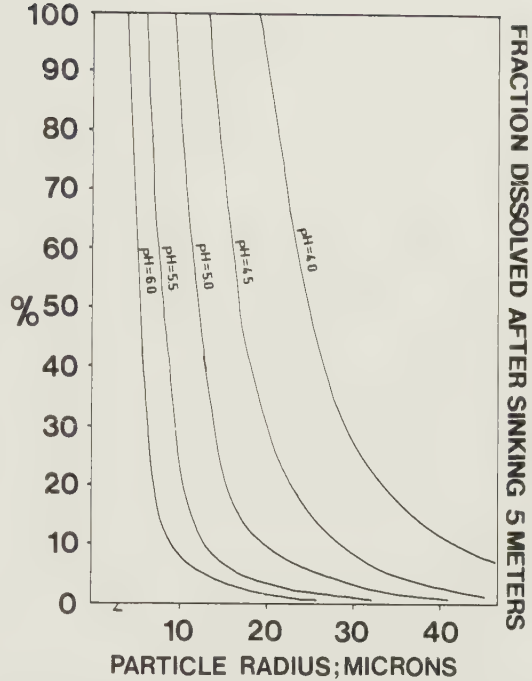


Fig. 3. Dissolved fraction of a particle that has sunk 5 m is plotted vs. particle diameter for different pH-values. Particles larger than 60 μm in diameter are only dissolved to a very little extent and will accordingly be of little use for lake liming.

$$\dots + (-1)^n \cdot \left(1 + \sum_{j=i-1}^1 \dots \left(\sum_{j=i-1}^{n-2} \left(\sum_{j=i-1}^{n-1} j \right) \right) \dots B^n \right). \quad (21)$$

This is the equation which describes the dissolution of an amount of sinking calcite powder, when the gradual decline in the hydrogen ion concentration is considered.

If by any chance all particles should sink in water of the same pH-value, perhaps induced by horizontal currents, the absolute maximum degree of dissolution is given by eq. (21);

$$X = A' \cdot H^+ \cdot S \cdot \sum_{i=1}^n \frac{\Delta\phi_i}{R_i^3} \quad (22)$$

and if all particles are of the same size in addition:

$$X = \frac{A' \cdot H^+ \cdot S}{R_0^3} \quad (23)$$

The equations are valid for particles larger than 10 μm and smaller than about 100 μm . Particles smaller than 10 μm are dissolved substantially faster than this theory predicts, particles larger than 100 μm will dissolve substantially slower.

For particles with radius smaller than 5 μm is the mass transfer coefficient dependent on the particle radius:

$$K_M = \frac{D}{R} \quad (24)$$

and the differential equation becomes eq. (24):

$$\frac{dX_1}{dS} = \frac{E}{R_1^4} (1 - X_1)^{-1/3} \cdot \Delta H^+ \quad (25)$$

$$\frac{dX_2}{dS} = \frac{E}{R_2^4} (1 - X_2)^{-1/3} \left(\Delta H^+ - \frac{M^*}{P \cdot M_E \cdot S} X_1 \right) \quad (26)$$

$$\begin{aligned} & \vdots \\ & \vdots \\ \frac{dX_n}{dS} &= \frac{E}{R_n^4} (1 - X_n)^{-1/3} \left(\Delta H^+ - \frac{M^*}{P \cdot M_E \cdot S} \right. \\ & \quad \left. \times (X_1 + X_2 + \dots + X_{n-1}) \right) \end{aligned} \quad (27)$$

where

$$E = \frac{10.125 \cdot \mu \cdot D_{H^+}^0}{\rho_P (\rho_P - \rho) g} \quad (28)$$

This equation is of little practical interest, because the conditions during most lake liming are such that the fraction of particles less than $10 \mu\text{m}$ will in any case dissolve completely. The general differential equation becomes

$$\frac{dX}{dS} = E \sum_{i=1}^n \frac{\Delta \phi_i}{R_i^4} (1 - X)^{-1/3} \cdot \left(\Delta H^+ - \frac{M^*}{P \cdot M_E \cdot S} \sum_{j=i-1}^{n-1} X_j \right) \quad (29)$$

with the initial condition for eqs. (14) and (29):

$$X = 0 \quad S = 0 \quad (29a)$$

The equation:

$$X = \left(\frac{3}{2} \cdot E \cdot \Delta H^+ \cdot S \cdot \sum_{i=1}^n \frac{\Delta \phi_i}{R_i^4} \right)^{3/2} \quad (30)$$

represents the homogeneous solution of the differential equation and the dissolution of one single particle falling alone. Equation (30) indicates that if there is no overdosage of smaller particles, then they can be considered to dissolve instantaneously.

Any value of $X > 1$ indicates that all particles have been dissolved before they reached the lake bottom.

If lake liming is carried out in a reasonable way, it can be assumed that excessive overdosage of calcite will not occur, and the dissolution will take place far from the saturation concentration for calcite. This allows us to assume that particles smaller than $10 \mu\text{m}$ in diameter will dissolve completely and that the residue will be dissolved according to eq. (19):

$$X = A' \cdot \Delta H^+ \cdot S \cdot \sum_{i=1}^n \frac{\Delta \phi_i}{R_i^3} (1 - P_i(B)) \quad (19)$$

where

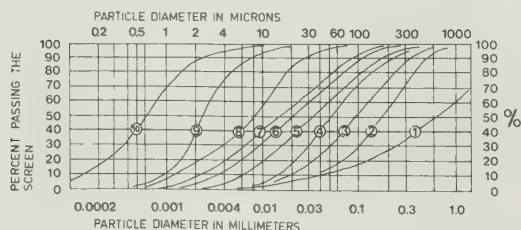


Fig. 4. The calcite powders listed in Table I have these screen analysis curves. Such curves should be determined by accurate methods such as sedimentation, coulter counter or wet sieving. Dry sieving will not do.

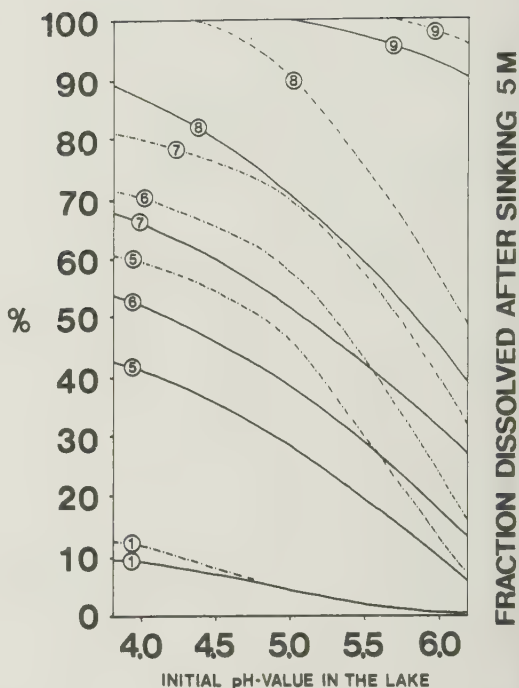


Fig. 5. The dotted line is the dissolved fraction vs. initial pH-value in the lake according to eq. (21) which does not take into account that the pH-value rises during the process. This represents an absolute maximum of what can be achieved in lake liming. The line is the average dissolved fraction for a lake liming with perfect cover of the whole lake area and no excessive dosage of calcite. The figures refer to the screen analysis curves and Table I.

$$B = \frac{A' \cdot M^*}{P \cdot M_E}$$

From eq. (19) it can be seen that for a given acidified lake, the liming result in terms of calcite utilization is determined by the following parameters:

$\sum_{i=1}^n \frac{\Delta \phi_i}{R_i^3}$: The inverted volume specific average radius for the powder used. An increase in the content of smaller particles will increase the fraction dissolved.

S : The mean depth of the area of the lake which is treated. A greater depth will increase the dissolved fraction.

M^* : The dosage of calcite powder per lake area for the whole lake. As long as M^* does not exceed the neutralization need, it has little effect on the dissolved fraction X .

P : The fraction of lake area treated. Due to the term M^*/P in eq. (30); a smaller P or fraction of the lake treated, increase local overdosage and decrease X . Accordingly, P should be as large as possible, the very best being 1.0.

Figure 3 shows eq. (23) plotted as dissolved fraction vs. particle radius for different pH-values. The values are for a depth of 5 m. It becomes quite clear from the diagram that

particles with radius larger than 40µm will hardly ever be of any use in lake liming.

With the help of a differential or, as in Fig. 4, a cumulative screen analysis diagram, the expression $\sum_{i=1}^n \Delta\phi_i/R_i^3$ can be estimated and the eqs. (21) and (22) calculated and plotted. They are shown in Fig. 5. The dissolved fraction is plotted vs. initial pH in the lake, which is 5 m deep. The dotted line represents eq. (22) and the line eq. (21). The figures on the curves indicate what screen analysis curve it corresponds to. If only a small fraction of the total lake surface area and volume are treated or excessive overdoses applied, then the calcite will dissolve to a far less fraction than this diagram indicates. The diagram can be used for other depths than 5 m by using the formula:

$$pH_{DIAGRAM} = pH_{LAKE} - \log_{10} \left(\frac{S}{5m} \right) \tag{31}$$

Actual liming costs

The brutto delivery price for the calcite used for lake liming is of minor interest. Depending on the method of application and type of calcite powder, the price for putting a certain amount into solution will vary a great deal. This implies that the cost for the desired result should be expressed as cost per ton dissolved. It can be calculated from the brutto delivery cost and the fraction dissolved in the operation. If the actual liming cost is called K_{EFF} , the brutto delivery price per ton for the calcite used K_{BRUTTO} , we have:

$$K_{EFF} = \frac{K_{BRUTTO}}{X} \tag{32}$$

In Table I the prices for the calcite powders shown in Fig. 4, are listed. The prices are per ton calcite distributed over the lake surface. If we combine these with the X-values from Fig. 5, Fig. 6 can be produced. It shows the actual cost per dissolved ton, vs. the initial pH-value in the lake for different calcite powders.

The dotted lines are cost lines for olivine and dolomite for comparison. Olivine is marked with O, and dolomite with D. The number indicate to which screen analysis curve they correspond.

Table I.

Commercial trade name	Screen analysis No.	Assumed calcite cost per metric ton, delivered on the lake surface; Sw. kronor
0-3 mm limestone gravel, Limhamn, Sweden	1	150:--
0-1 mm limestone powder Ignaberga, Sweden	5	200:--
0-0.5 mm limestone powder Köpinge, Sweden	6	230:--
0.0-2 mm limestone powder Köpinge and Ignaberga, Sweden	7	280:--
0-0.04 mm limestone powder Köpinge, Sweden	8	380:--
0-0.016 mm Chalk powder Malmö, Sweden	9	800:--
0-0.002 mm Marble powder Carbital 90, Italy	10	600:--

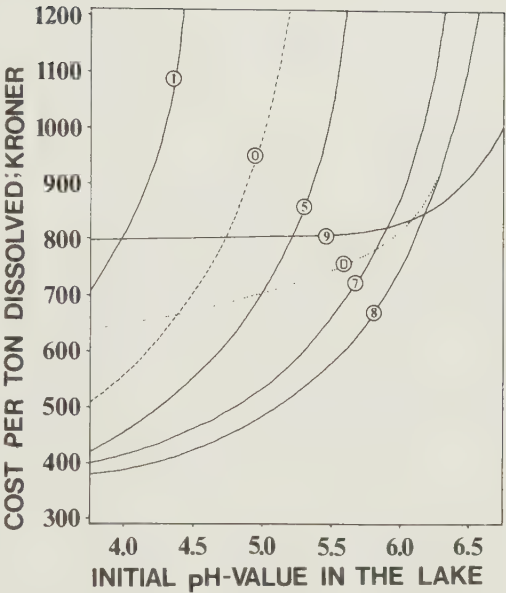


Fig. 6. The diagram shows a plot of the cost function. In it the effective liming cost per dissolved calcite can be read for some of the calcite powders. The line marked D is for dolomite powder with the same screen analysis curve as calcite powder No. 8. O represents the line for an olivine powder with the same screen analysis curve as dolomite. It becomes quite clear that the finer calcite powders offer the best economy in a lake liming project.

1: 0-3.0 mm calcite. 5: 0-1.0 mm calcite. 7: 0-0.2 mm calcite. 8: 0-0.044 mm calcite, 9: 0-0.016 mm calcite. O: 0-0.044 mm olivine. D: 0-0.044 mm dolomite.

Conclusions

The data in the reports from lake liming projects are not always clear enough or sufficient for an analysis of the actual neutralization cost and calcite utilization. But a number of reports contain data enough to estimate the fraction dissolved calcite of what was added in the water. As the liming was carried out over various depths of the lakes, the data are adjusted with eq. (31) to their 5 m depth equivalents. They are shown in Fig. 8 together with the theoretical lines. It can be seen that the observed data agree well with the theoretical predictions.

When the amount dissolved during sinking is compared with the whole amount dissolved in a project over a number of years, a close look on the reports will show that there is no great difference between soil liming and the calcite lying on the bottom of a lake. There are no indications that water movements in the littoral zone of the lake will suffice to increase the dissolution rate or erode the calcite particles. This can be seen particularly clearly in the liming of several small lakes in the Grytsjön area, in the Finspång river system, which were only limed on the beaches and in very shallow water. Hardly any calcite ever dissolved during sinking and the calcite was rapidly inactivated on the bottom.

A large improvement in neutralization costs and calcite utilization can be achieved if liming of shallows and littoral zones only, can be changed and as much as possible of the

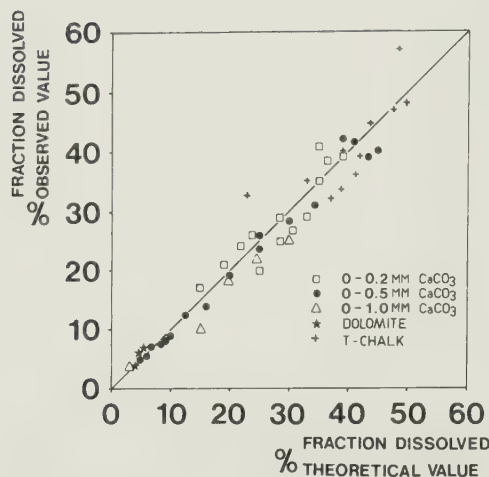


Fig. 7. The theoretical prediction for dissolved fraction plotted vs. the observed value in 40 lake-liming projects in Sweden. The observed values verify the predictions to within $\pm 8\%$ of the observed value.

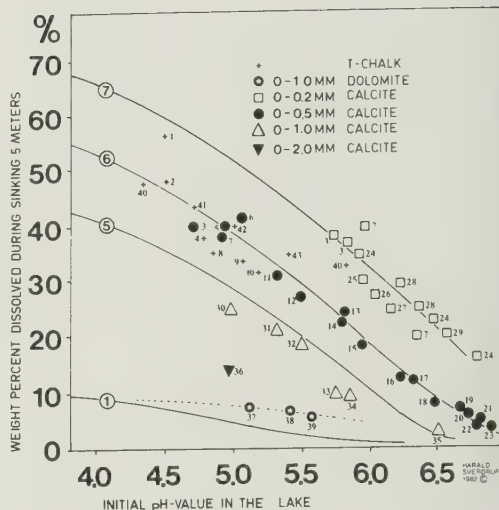


Fig. 8. The figure shows the fraction dissolved of different calcite powders while sinking to the bottom. As the lake depth was different in the various liming projects, all values are adjusted to a depth of 5 m according to eq. (31):

$$\text{pH}_{\text{Adjusted}} = \text{pH}_{\text{Lake}} - \log_{10} \left(\frac{\text{Lake depth}}{5.0 \text{ m}} \right) \quad (31)$$

In the reports from The Swedish Environmental Protection Board and from the National Board of Fishery, the calcite powders were classified as follows: 0–0.2 mm calcite powder; 0–0.5 mm calcite powder; 0–1 mm calcite; 0–1 mm T-chalk; 0–3 mm dolomite powder. The data marked 23 through 26 are partially based on data concerning alkalinity. The lines reflect the predictions of the theories for the calcite powders classified as 1, 5, 6 and 7 in the screen analysis diagram. The data were provided by the National Board of Fisheries at Gothenburg.

- | | | |
|-----------------------|---------------------|------------------------|
| 1: Eigdesjön | 16: Västersjön | 31: Nedra Särnamansjön |
| 2: Nordre Blötevatten | 17: Stora Ullen | 32: Tvärvattnet |
| 3: Barken | 18: Ölen | 33: Grössjön |
| 4: Övre Bolsjön | 19: Eskiltorpasjön | 34: Nätsjön |
| 5: Hornsjön | 20: Visslösjön | 35: Visnen-Opperhalen |
| 6: Stora Härsjön | 21: Grytsjön | 36: Upprämen |
| 7: Högsjön | 22: Bosjön | 37: Silken |
| 8: Sörvammssjön | 23: Uppsala | 38: Långetjärn |
| 9: Söndra Blötevatten | 24: Hjärteredsjön | 39: Stora Kumlan |
| 10: Hosjön | 25: Vällsjön | 40: Lysevatten |
| 11: Lilla Härsjön | 26: Tjurken | 41: Bredevatten |
| 12: Blomman | 27: Silo, Högvadsån | 42: Skitjärn |
| 13: Annebergsjön | 28: Multen | 43: Stensjön |
| 14: Ekelidvattnet | 29: Kullsjön | |
| 15: Stora Malen | 30: Smedevattnet | |

lake area could be limed instead. This would greatly improve the direct effect and the long term dissolution from the bottom as well. This is because a substantially larger part of the water volume comes in direct contact with the calcite during sinking, and on the bottom the area of contact between wet and solid will be larger. Some of the projects like Lake Barken or Bolsjön, show this.

Figure 8 shows that particle size is essential, and that the finer powders always give much better calcite utilization. This fact becomes increasingly important as the initial lake pH rises above pH 5.5. A test of the theory can be seen in Fig. 7 where the predicted values are plotted vs. the observed values of X from 43 liming projects.

It can be summarized as follows: The calcite powder should in all cases be spread over as much as possible of the lake area, regardless of what the bottom underneath would look like, Finer calcite powders should be preferred to coarser ones, especially at initial lake pH-values above 5.5. Powders coarser than the screen analysis curve, marked 5, will always give low calcite utilization.

Concerning calcite on the bottom of a lake

Calcite, resting on the bottom of a lake, has, due to the hydrodynamic conditions, a very low dissolution rate. In most cases it gets inactivated on the surface and buried in the sediment quite rapidly. This leads to the fact that the calcite, resting on the bottom may well have an effect on the lake, but this effect is out of proportion compared to the amount of calcite invested. In all lake liming the amount on the bottom should be minimized as compared to the amount dissolved during sinking time. An experimental study and the exact equations concerning dissolution from the bottom will be presented elsewhere.

Acknowledgements

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This study has been carried out at the Department of Chemical Engineering at The Lund Institute of Technology under the supervision of Professor Ingemar Bjerle.

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Dissolution of Calcite Powder Sinking in a Column of Acid Water in Relation to a Theoretical Lake Liming Model

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Abstract

Dissolution experiments with calcite powder sinking into stagnant column of acidic water shows that this can be described with a mathematical model, and hence provide the Swedish liming projects with a valuable tool for planning. The study also showed that dry application will give only 50% of the theoretical result, which can easily be produced with wet slurried calcite powder.

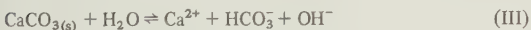
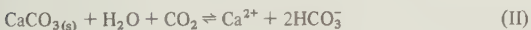
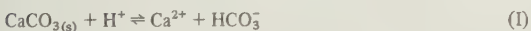
Introduction

In earlier works concerning the dissolution kinetics of calcite, a model for the dissolution of a calcite, sinking in an acidic aqueous solution, has been developed. The resulting differential equation has been solved both analytically and numerically for a number of situations, and has been verified with data from a large number of Swedish Lake liming projects (Sverdrup [1]).

As many of Sweden's decision makers and researchers on acidification mitigation are inexperienced in theoretical and experimental chemistry, as well as sceptical towards theoretical studies, it was decided to do additional experiments under very controlled conditions to verify the theoretical calculations.

Dissolution of calcite in natural lake water

The dissolution of solid calcite in dilute acid can be described as a heterogeneous solid-liquid reaction. The chemical reactions involved are:



In natural lake waters with a pH-value less than pH 6.5, reaction (i) will dominate, and for pH-values above 6.5, reaction (III) will play an important role. In most cases the lakes considered in this study will contain too little dissolved CO_2 for reaction (II) to be of any importance.

In lake liming we operate in the range from pH 4.0 to pH 6.5, and within this range reaction (I) dominates. Under these conditions the dissolution rate is linearly dependent on the hydrogen ion concentration, and the process controlled by the diffusion of this ion. It can be described with mass transfer models following the principles outlines by Sherwood *et al.* [2] and by Crank [3].

Theory

When a calcite powder is spread in a lake, the particles will rapidly be distributed according to size, sink through the water column, and dissolve. This process has been described earlier in detail in Sverdrup and Bjerle [4] and Sverdrup [1]. The dis-

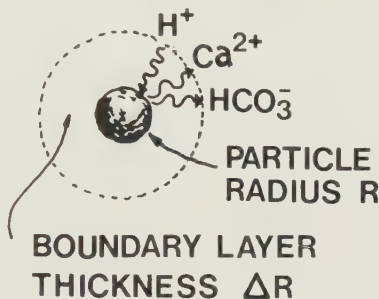


Fig. 1. The dissolution rate is limited by the diffusion of reactants from the liquid into the solid surface.

solution process is controlled by the diffusion of the hydrogen ion, and, for the dissolution of one particle as in Fig. 1 the governing equation may be written

$$-\left(\frac{\partial M_j}{\partial t}\right) = D \left(\frac{\partial [\text{H}^+]}{\partial R_j}\right)_{R_j} A_j M_e \quad (1)$$

The interpretation of this equation is that the mass dissolved is proportional to the flux of hydrogen ions into the surface A_j of the particle with the radius R_j .

If a powder, composed by many different particle sizes and sinking through the water column as in Fig. 2, is considered, we get the differential equation

$$-\frac{d}{dS} \left(\sum_{i=1}^n M_i \right) = A \sum_{i=1}^n \frac{\Delta \phi_i}{R_{0i}^3} \left(\Delta H - \sum_{j=i-1}^{n-1} \frac{M_0 - M_j}{A_L P M_E} \right) \quad (2)$$

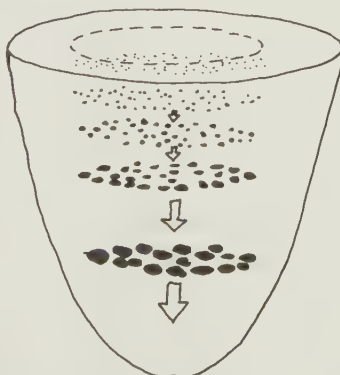


Fig. 2. Visualization of the sinking-dissolving model for lake liming.

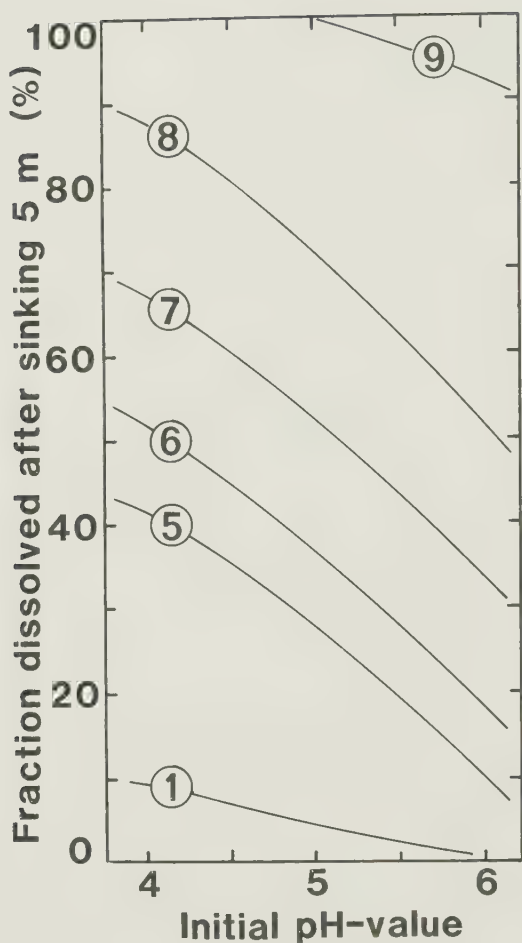


Fig. 3. Dissolution curves for different slurried calcite powders sinking in acidic water. The diagram may be used for other depths than 5 meter if the initial pH-value is adjusted using the formula diagram $\text{pH} = \text{initial pH} - \log_{10} (\text{depth}/5 \text{ m})$. The lines correspond to different grades of calcite powder which are defined in Fig. 4. Numbers 6 and 7 are the most commonly used powders in Swedish lake liming.

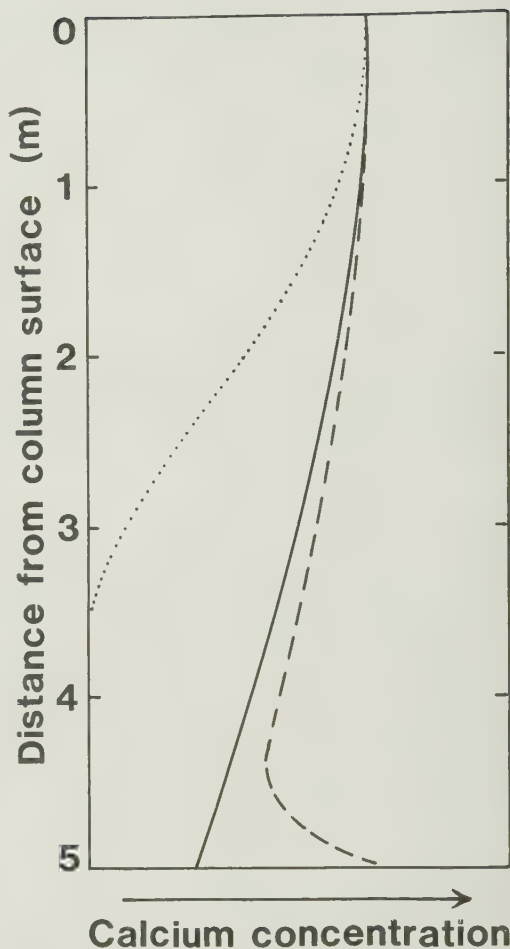


Fig. 4. The calcium concentration profile through the column develops with time as shown. The dotted line (· · ·) indicate the profile after 2 h. After 25 h, the profile may be described by the dashed line (---). It can be seen how some of the calcite on the bottom of the column is slowly dissolved. The full-drawn line (—) was used when evaluating the experiments.

The equation may be solved by hand calculations through a sum of asymptotic solutions and back iteration to correct the change of the hydrogen ion concentration, as well as numerically with a small computer. Both ways can be shown as solution diagrams as in Fig. 3. The analytical solution may be derived in the interval pH 2.5–5.5 for systems low in CO_2 :

$$X = A' \Delta H S \sum_{i=1}^n \frac{\Delta \phi_i}{R_{0i}^3} \left\{ 1 + \left(1 + \sum_{j=i-1}^{n-1} j \right) B \right. \\ \left. + \left[1 + \sum_{j=i-1}^{n-2} \left(\sum_{j=i-1}^{n-1} j \right) B^2 \dots + (\cdot 1)^n \right] \right. \\ \left. \times \left(1 + \sum_{j=i-1}^1 \dots \left(\sum_{j=i-1}^{n-2} \left(\sum_{j=i-1}^{n-1} j \right) \right) \dots \right) B^n \right\} \quad (3)$$

and the dosage factor B

$$B = \frac{AM^*}{M_e P} \quad (4)$$

For other conditions ΔH may not be only dependent on H^+ -ion alone but may be expressed as

$$\Delta H = K_1[\text{H}^+] + K_2[\text{CO}_2] + K_3 - K_4[\text{Ca}^{2+}][\text{CO}_3^{2-}] \quad (5)$$

The handling of the equation and the values of the constants are given by Plummer [5].

Experimental design

The experiments were carried out in a 5 m deep metal column 20 cm in diameter. The value was around 150 l. Through small membranes samples could be collected with a syringe along the column.

For the experiments, the acidic aqueous solution was prepared from sulfuric acid in order to obtain maximum similarity with acid lakes. As shown by Sverdrup and Bjerle [4] the potential problem with precipitation of CaSO_4 on the calcite surface can be neglected at pH-values exceeding 1.5.

Inaccuracy can occur as particles on the bottom of the column partially may dissolve, while other smaller particles are still on their way to the bottom.

How the calcium concentration profile develops with time appears in Fig. 4. It can be seen how the particles penetrate the column as well as how the particles dissolving from the bottom affects the profile. An intermediate profile, corresponding to the full drawn line in Fig. 4 was used for the evaluation.

The calcium concentration was determined by titration with EDTA. The accuracy was $\pm 0.1 \text{ mg l}^{-1}$ or approximately $\pm 2\%$.

The calcite slurry was prepared by suspending the powder into a few ml of water, and was distributed as droplets over the column surface. Immediately thereafter, the top few centimeters of the column was stirred gently, and thus the powder was spread evenly over the whole area. This procedure did not seem to disturb the downward motion of the calcite particles.

As the top section of the column was transparent, one could see how the powder was separated very rapidly into fractions with different downward velocity, as outlined in Fig. 2.

In experiments where dry powder was used the meal was sieved through a 0.2 mm grid over the surface. This was followed by gentle stirring as described above.

Results versus the mathematical model

Experiments were performed with limestone powders, classified as 0-0.2 mm with a particle size distribution corresponding to No. 7 in Fig. 5, and 0-0.044 mm, represented by curve No. 8.

The results from 8 sets of experiments are shown in Fig. 6. The dashed lines represent model calculations based on the assumption that the dissolution is solely H^+ -ion dependent, thus

$$\Delta H = K_1[\text{H}^+] \quad (6)$$

The experiments show that this assumption is reasonable at initial pH-values less than 5. At higher values however, the

dissolution will also depend on the carbon dioxide present in the solution and the direct attack of water molecules. If this, and the back reaction near the saturation point are accounted for we get good agreement between experiments and model calculations, the full-drawn line in Fig. 6. The kinetic expression is thus

$$\Delta H = K_1[\text{H}^+] + K_2[\text{CO}_2] + K_3 - K_4[\text{Ca}^{2+}][\text{CO}_3^{2-}] \quad (5)$$

The importance of dose intensity

The dose intensity is expressed as amount calcite per limed surface g m^{-2} or in amount per cubic meter of water.

The results from experiments with 0-0.2 mm grade limestone at pH 4.0 is shown in Fig. 7. It can be seen that the dissolved fraction falls off faster with increasing dosage than the theory predicts. We can speculate about two reasons for this.

One reason may be a phenomenon called "Ostwald ripening". (McCabe and Smith [6]). Thermodynamically the difference between a very small particle and a larger one is that the small particle possesses a significant amount of surface energy per unit mass and the large one does not. One consequence of this difference is that the solubility of a small crystal in the less than micrometer range, is larger than of the large crystal. A small crystal can be in equilibrium with a supersaturated liquid. Such an equilibrium is unstable if larger crystals are present. The smaller crystal will dissolve and the larger will grow until the smaller eventually disappears.

For a solution, the chemical potential will be

$$\mu = \mu^* + RT \ln [\text{Ca}^{2+}][\text{CO}_3^{2-}] \quad (7)$$

and the solubility product K_s

$$-\ln K_s = \frac{\mu^*}{RT} \quad (8)$$

as the chemical potential of the solution at the particle surface will be equal to zero at equilibrium.

For very small particles in equilibrium with the solution, an energy term has to be added for the additional surface energy potential μ_s

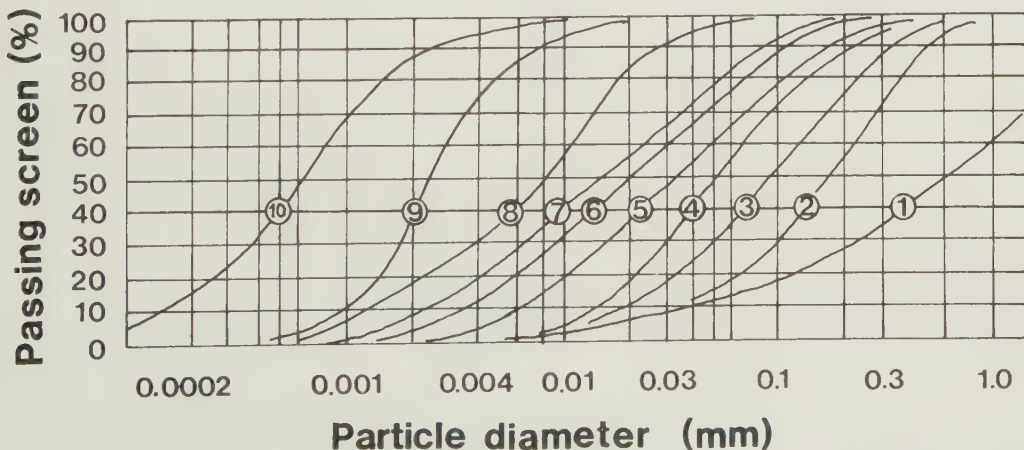


Fig. 5. Particle size distribution curves for different grinding grades of calcite powders used in Sweden. Their commercial classification are: 1: Agricultural limestone 0-3 mm, 5: Agricultural limestone 0-1 mm,

6: Lake liming powder 0-0.5 mm, 7: Lake liming powder 0-0.2 mm, 8: Extra fine powder 0-0.044 mm, 9: Filler calcite powder 0-0.005 mm.

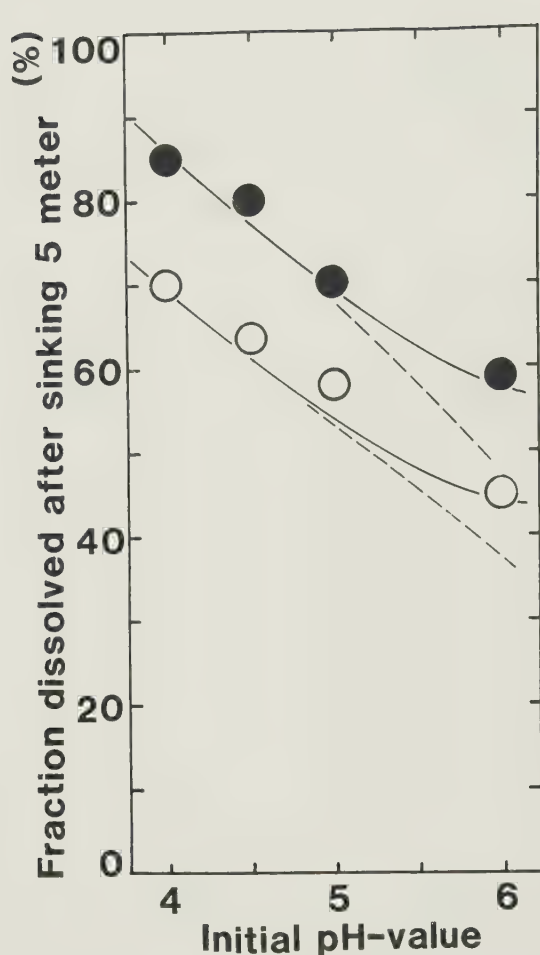


Fig. 6. The result of 8 sets of experiments are shown together with the theoretically calculated dissolution curves for powders No: 7, $\circ$, and No. 8, $\bullet$. Dashed lines correspond to calculations based on the assumption that the H^+ ion alone dominates the dissolution reaction, as in eq. (6). Full-drawn lines represent calculations according to the full expression [eq. (5)].

$$\mu + \mu_s = \mu^* + RT \ln [Ca^{2+}][CO_3^{2-}]$$

and the solubility at the surface

$$-\ln K_s = \frac{\mu^* - \mu_s}{RT}$$

It can be seen that the solubility at the surface of calcite particles increases with the surface energy.

In the equation for the reaction rate:

$$\Delta H = K_1[H^+] + K_2[CO_2] + K_3 - K_4[Ca^{2+}][CO_3^{2-}] \quad (5)$$

the mass transport from the smaller particles to the larger ones will strengthen the last term considerably if the solution is approaching the saturation point. This will be more pronounced at pH values above 5 where the influence of the hydrogen ion

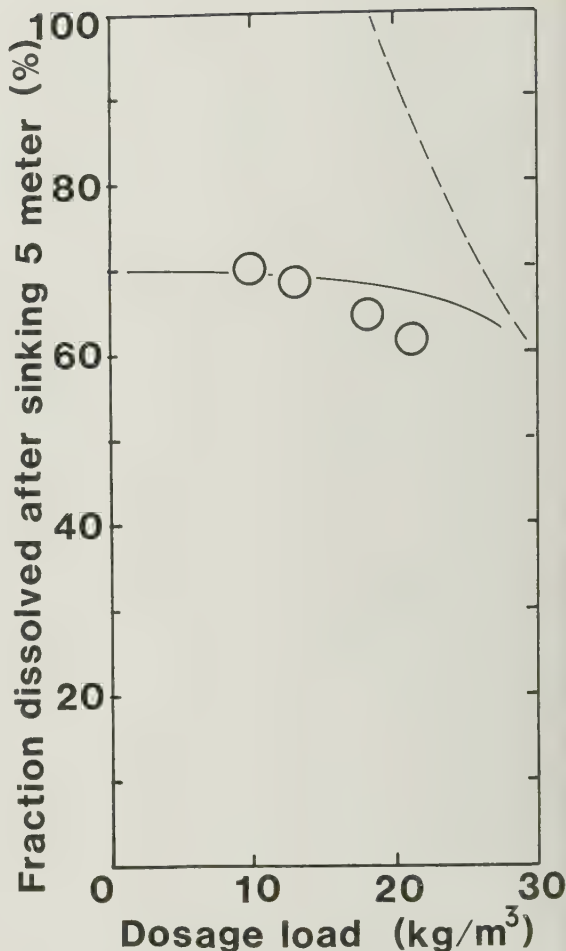


Fig. 7. The dissolved fraction falls off rapidly at doses exceeding 15 g m^{-3} as the saturation point (---) then is approached. Although the model does account for the backward reaction according to eq. (5) it is not valid for doses in this range.

is less dominant. At very high dosages local saturation occurs during the liming.

- (9) Another possibility is that at higher dosages the particles more easily could form aggregates during sedimentation.

The importance of wet slurried powder versus dry application

In earlier works we have shown that the smaller particles in a dry powder of calcite will adhere to the surfaces of the larger ones (Sverdrup and Bjerle [4]). This may be seen in Fig. 8.

The evaluation of lake limings performed in the years 1977 to 1980 indicated that the calcite did dissolve to a somewhat lesser extent when it was applied dry, as compared to when it was slurried in water and then distributed.

Figure 9 shows the results of experiments with calcite powder applied as dry powder, as well as powder that was well mixed in a few ml of water and spread as a slurry. The results show very clearly that calcite powder prepared to a well

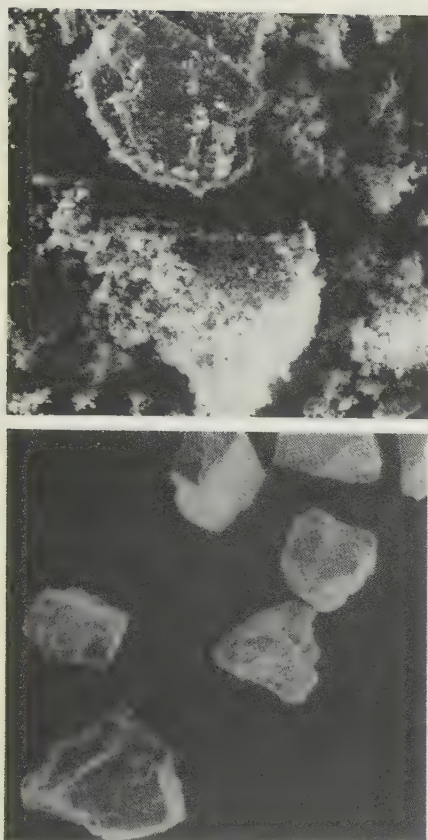


Fig. 8. Two micrographs (600X) showing a dry powder and wet slurried particles. It can be seen that small particles will adhere to the larger ones in a dry system. Slurrying will separate the particles from each other.

stirred slurry prior to distribution is important for the dissolution.

If it is assumed that the reduction in fraction of the powder dissolved is caused by loss of the finer particles, it implies that all particles smaller than 6 microns will "ride" with the larger ones towards the bottom. This is consistent with what can be seen in Fig. 8 (Sverdrup *et al.* [7]).

Discussion

The results show that the dissolution of a slurried calcite powder, sinking in a water column, can be described with a mathematical model. This is confirmed by earlier studies (Sverdrup [1]). The model should be a very useful tool when lake liming is planned.

The fact that dry application only gives 50% of the dissolution achieved by wet application should arouse planners to think twice when liming operations are designed. Experiences from dry dosing into running waters and from airborne lake liming stress the importance of careful slurrying of the calcite before it is spread into the water.

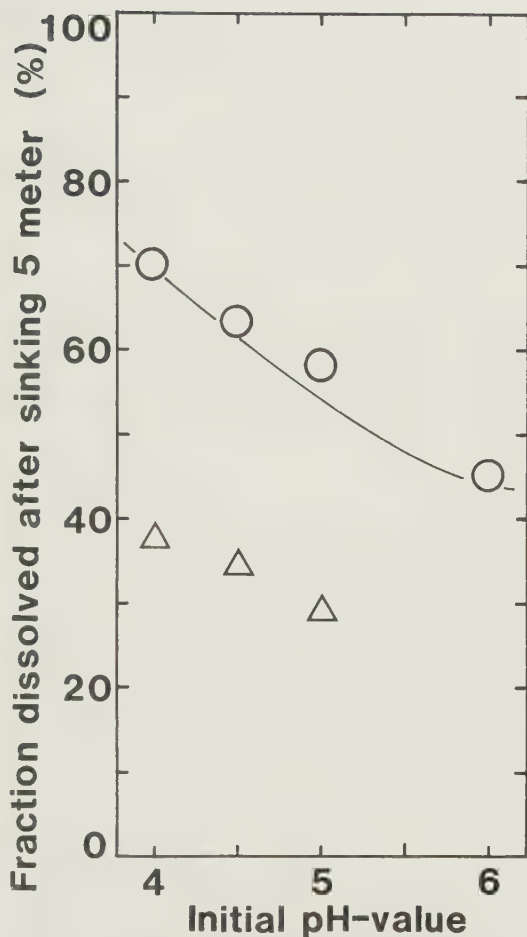


Fig. 9. The diagram shows the large difference in dissolution efficiency between a wet slurried powder, ○, and dry application, △, of calcite powder classified as 0–0.2 mm.

List of symbols

A_j	Particle surface area	$[m^2]$
A	Integration constant	
A'	Integration constant	$A' = A/M_0$
A_L	Lake surface area	$[m^2]$
B	Dosage intensity factor	
$[Ca^{2+}]$	Calcium concentration	$[kmol\ m^{-3}]$
$[CO_2]$	Carbon dioxide concentration	$[kmol\ m^{-3}]$
D	Diffusion coefficient	$[m^2\ s^{-1}]$
ΔH	Dissolution driving force	$[kmol\ m^{-2}\ s^{-1}]$
$[H^+]$	Hydrogen concentration	$[kmol\ m^{-3}]$
i	Index	
j	Index	
K_i	Diffusion or reaction rate coefficient	$[m\ s^{-1}]$
K_s	Solubility product	$[kmol^2]$
M_0	Initial mass	$[kg]$
M_j	Mass of fraction j in the particle distribution	$[kg]$

n	Number of particle fractions	
M^*	Dosage load	$[\text{kg m}^{-2}]$
M_e	Ekivalent mass	$[\text{kg mol}^{-1}]$
P	Fraction of the lake area limed	
R_i	Radius of particle i	$[\text{m}]$
R_{0i}	Initial radius of particle i	$[\text{m}]$
R	Universal gas constant 8.31 kJ mol^{-1}	
S	Lake depth, sinking depth	$[\text{m}]$
T	Absolute temperature	$[\text{K}]$
X	Fraction dissolved	
$\Delta\phi_i$	Fraction of particles in class i	
μ^*	Chemical potential of the pure substance	$[\text{MJ kmol}^{-1}]$
μ_s	Surface energy potential	$[\text{MJ kmol}^{-1}]$
μ	Chemical potential	$[\text{MJ kmol}^{-1}]$
$(\partial c/\partial R)_R$	Concentration gradient at the particle surface	$[\text{kmol m}^{-4}]$

$(\partial M_j/\partial t)$	Dissolution rate	$[\text{kmol s}^{-1}]$
$\Sigma_{i=1}^n a_i$	Sum of all elements a_i for $i = 1$ to n ;	$a_1 + a_2 + a_3 + \dots + a_n$

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A Simple Model for the Reacidification of Limed Lakes, Taking the Simultaneous Deactivation and Dissolution of Calcite in the Sediments into Account

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Abstract

In lake liming operations in Sweden, it has been common practice to use calcite powder to neutralize acidified lake waters, and to deliberately place an amount of calcite on the lake bottom to get long term dissolution.

In this report we intend to show that the calcite placed on the bottom, will be able to influence the lake chemistry only for a limited period of time. Calcite on the lake bottom will, in addition to being covered by sedimentation, become inactivated by precipitates of humus and clay minerals clogging the calcite surfaces.

In a first approximation the active calcite surface area can be described with the expressions similar to those describing catalyst deactivation. The decreasing active calcite surface area can be described with an exponential expression.

In a first approach the lake was modelled as a continuously stirred tank. The equations were derived from a mass balance to describe the long term development of pH, alkalinity and calcium concentration in the lake.

For special cases of constant flow rate or load, analytical solutions have been derived. In other cases the solutions were calculated numerically from the differential equations.

The model has been tested for a number of Swedish limed lakes, and seems to describe the reacidification of a limed lake fairly well.

Both the model and the data sets indicate that the calcite on the bottom of a limed lake inactivates, and has little effect on the lake water chemistry after approximately two years.

Introduction

Thousands of lakes and rivers in Scandinavia and North America located on low weathering bedrock or surrounded by soils with a low calcite content are suffering from the effects of acid rain.

In Norway and Sweden waters in the southern parts of the countries, an area of almost 200 000 km², will have critical pH-values during some time of the year.

Nearly forty thousand lakes are affected, in addition to countless kilometers of rivers and brooks.

The measure most frequently taken is applying calcite in different ways to the river or lake affected. This is in fact the only large scale remedy available until emissions of SO₂ and NO_x have been reduced drastically on the European continent.

In Sweden large programs for liming of lakes and running waters are in progress and despite the stressed state finances, about 200 million Swedish kronor will be spent each year in the final program. In Southern Sweden the total amount needed for neutralization is estimated to about 800 000 tons of calcite each year. It is quite obvious that it is of great importance to use the resources as efficiently as possible. The desired result of liming of lakes and running waters is that every cubic meter treated achieves a good pH-value and alkalinity. This is achieved by dis-

solving at least the amount needed for neutralization of the acidic water. The fraction not dissolved is of no interest and is lost or wasted. Accordingly, the total neutralization cost depends not only on calcite cost but on fraction dissolved as well.

1. Dissolution of calcite

Acidified lakes in Sweden are reclaimed by adding calcite powder to the lakes. This neutralizes the acid and restores the alkalinity. A large fraction of the calcite dissolves during sinking, and the rest precipitates on the bottom. This study concerns the dissolution of calcite from the bottom and the process of reacidification.

In earlier studies we have treated the dissolution of calcite; Sverdrup and Bjerle [1], and in connection with lake liming; Sverdrup [2, 3], Sverdrup and Bjerle [4] and the transport of substances from the bottom sediments: Warfvinge and Sverdrup [5] and liming of running waters, Sverdrup *et al.* [6, 7].

The dissolution of calcite in dilute acidic water can be described as a heterogeneous solid-liquid reaction controlled by diffusion. The chemical reactions involved are [8]



In natural waters with a pH-value below 6 and a carbon dioxide partial pressure less than 0.3 atm, reaction (I) will dominate, and the dissolution rate will be proportional to the hydrogen ion concentration, while at higher pH-values reaction (III) will dominate. If the CO₂-partial pressure exceeds 0.3 atm the reaction (II) will contribute to the dissolution, and the dissolution rate may be increased as much as two orders of magnitude [9].

The backward reactions can be shown to be dependent on the HCO₃⁻ concentration, and for the dissolution rate the general equation is:

$$R = k_1[\text{H}^+] + k_2[\text{CO}_2] + k_3[\text{H}_2\text{O}] - k_4[\text{Ca}^{2+}][\text{HCO}_3^-] \quad (1.1)$$

In this study acidified lakes in the pH-range pH 4 to pH 7 and at low carbondioxide partial pressures, are studied. This limitation reduces the kinetic expression to a simpler form at pH-values less than pH 6.0

$$R = k_1[\text{H}^+] \quad (1.2)$$

and between pH 6.0 and pH 7

$$R = k_1[\text{H}^+] + k' - k_4[\text{Ca}^{2+}][\text{HCO}_3^-] \quad (1.3)$$

The last term in the latter equation will take account of the backward reaction at high alkalinities [8].

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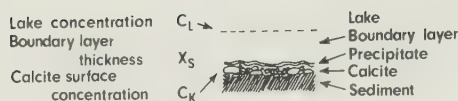


Fig. 1. The lake-sediment interface.

1.1. The ideal case: Dissolution without inhibiting effects

First we shall consider the ideal case in which no inhibition of the calcite surface takes place, and the dissolution is controlled by diffusion. We also have strong reasons to assume that biological activity, the so called bioturbation does not significantly influence the dissolution process [5, 10].

The equation for diffusion through a plane sheet is

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial X^2} \right) \quad (1.4)$$

As the times involved in lake systems are very long as compared to the chemical systems involved, we assume that a local pseudo-steady state exists, leading to the equation for the dissolution

$$-\frac{dM}{dt} = D \left(\frac{dC}{dt} \right)_{X_S} A_L P M_E \quad (1.5)$$

where $A_L P$ is the calcite surface area, expressed as a fraction P of the lake surface area.

The equation becomes for the overall dissolution

$$-\frac{dM}{dt} = R A_L P M_E \quad (1.6)$$

For very many situations it is sufficient to use the simplification mentioned earlier, that the hydrogen ion dominates the process

$$-\frac{dM}{dt} = K_M [H^+] A_L P M_E \quad (1.7)$$

where K_M is the mass transfer coefficient for the diffusion of hydrogen ions into the calcite surface.

This simplification with respect to the concentration will not introduce any large error, as we can assume that the liquid bulk concentration of hydrogen ion in the lake always will be several orders of magnitude larger than the concentration at the solid calcite surface.

The lake is taken to be well mixed and to have an initial hydrogen ion concentration C_0 , the tributaries have a feeding rate V^* with concentration C_{IN} . This assumption holds reasonably well as long as the theoretical residence time is longer than the mixing time of the lake. Most lakes are thoroughly mixed at turnover in the autumn and in the spring.

The mass balance for the lake of depth S and volume V and a fraction P of the bottom area covered with calcite becomes

$$V^* C_{IN} = K_M A_L P C + \frac{dC}{dt} V_L + V^* C \quad (1.8)$$

If it is assumed that the volume and the tributary flow rate are constant, then the retention time for the water in the lake is $T = V_L / V^*$, and eq. (1.8) can easily be rearranged to

$$\frac{dC}{dt} + \left(\frac{K_M P T}{S} + 1 \right) \frac{1}{T} C = \frac{C_{IN}}{T} \quad (1.9)$$

with the boundary condition:

$$t = 0 \quad C = C_0 \quad (1.10)$$

Table I. The final pH-elevation in the ideal case as a function of lake retention time and mass transfer rate from the sediments.

Mass transfer number $K_M P T / S$	Lake retention time in years			Final maximum pH-elevation in pH units
	A	B	C	
378	20	200	—	2.60
38	2	20	200	1.60
3.8	0.2	2	20	0.65
0.4	—	0.2	2	0.13

A: $K_M = 10^{-5} \text{ m s}^{-1}$, B: $K_M = 10^{-6} \text{ m s}^{-1}$, C: $K_M = 10^{-7} \text{ m s}^{-1}$.

The maximum concentration difference from the initial is given by the limiting case of eq. (1.9) at $t \rightarrow \infty$

$$\frac{C}{C_0} = \frac{C_{IN}}{C_0} \frac{1}{(1 + C_1)} \quad (1.11)$$

$$C_1 = \frac{K_M P T}{S} \quad (1.12)$$

In Table I, the maximum pH differences are listed vs. values of C_1 for a lake with tributaries having a pH value of 4.0. It can be seen that in the ideal case, only lakes with long retention times (many years), can benefit by calcite placed on the bottom to protect them against reacidification.

However, in reality, the problem becomes more complex. With the exception of a very few special cases, the dissolution rate will come to a very low level or a complete stop. The ideal system does not suffice to describe what is actually taking place, and only serves to give a maximum for what is hypothetically possible.

2. The inhibition of the calcite dissolution by the precipitation of humus complexes

Most natural waters contain various amounts of humics and compounds containing aluminium and iron. Their form and concentration are highly dependent on the pH-value of the water. At higher pH-values, as in a boundary layer over a calcite surface, many complexes and precipitates form that will settle on the calcite surface. Such a surface can be seen in the Scanning Electron Microscope photographs in Figs. 2 and 3. Energy-Dispersion X-ray studies shows that aluminium, silica

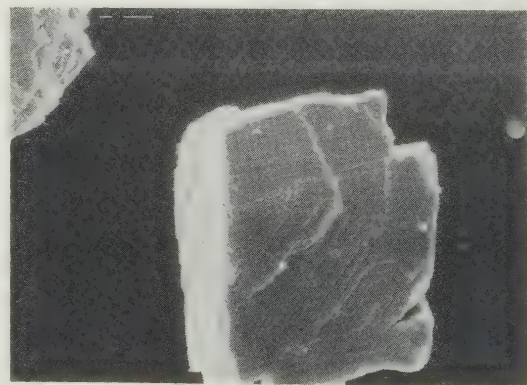


Fig. 2. Scanning Electron Microscope photographs of a fresh calcite particle in 600 times magnification.

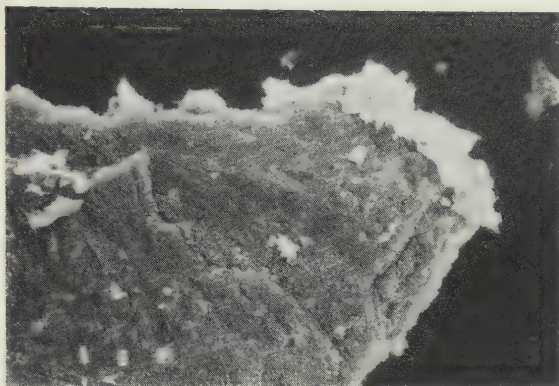


Fig. 3. Photographs of a calcite particle from the bottom of lake Tjurken. The calcite surfaces have been covered patchwise with precipitates.

and iron are present in the precipitates. The calcite particle was sampled from the bottom of a limed brook.

This fact becomes important in lake liming as the higher pH-value in the boundary layer near a calcite surface will cause the complexes to precipitate on the surface and thus inhibit the dissolution process. For particles sinking towards the lake bottom, the hydrodynamic conditions are such that no precipitation will occur. On the bottom, the boundary layer will be much larger and precipitation on the surface can take place.

There are two coupled mechanisms occurring simultaneously:

(a) The dissolution of calcite, and a subsequent rise in the pH-value due to neutralization of the acid.

(b) Due to the rise in the pH-value, precipitation of humus and metal complexes on the surface will occur, and the dissolution will be inhibited.

2.1. Theory of inhibition

It is assumed that the precipitation of inhibitor, that is the complexes of humus and metals, is proportional to the particle surface area available to dissolution. We can write the relation between the active surface area A and the inhibitor I being deposited on the calcite surfaces

$$\frac{dI}{dt} = K_P A \quad (2.1)$$

This causes the active surface area in turn to decrease

$$-\frac{dA}{dt} = K_D \frac{dI}{dt} \quad (2.2)$$

Assuming the dissolution to be dominated by the hydrogen ion concentration, we get

$$-\frac{dM}{dt} = K_{MA} [H^+] M_E \quad (2.3)$$

In this equation the product K_{MA} will decrease due to the inhibition, with the rate

$$R_i = \frac{d}{dt}(K_{MA}) \quad (2.4)$$

If we combine these equations we get

$$-\frac{d}{dt}(K_{MA}) = K_H(K_{MA}) \quad (2.5)$$

where

$$K_H = K_P K_D \quad (2.6)$$

When the equation is integrated we have two cases to consider. In the first case we have lakes with a low content of inhibitors as iron, aluminium and humus where the inhibition process will stop at a certain point. This may be the case for some of the lakes in the coastal regions of the Scandinavian peninsula and of the Norwegian high plateau.

For the first case integration will yield

$$K_{MA} = (K_{MA})_{t=0} e^{-K_H t} + (K_{MA})_{t=\infty} (1 - e^{-K_H t}) \quad (2.7)$$

The inhibition process does not kill the dissolution process, but stabilizes it on a lower level.

The second case deals with lakes with a high content of inhibitors, as most brown water lakes of the Scandinavian woodlands. In this case the supply of inhibitor is inexhaustible in relation to active limestone surface available on the bottom. The inhibition process will kill the dissolution process by blocking all active surface areas. We get

$$(K_{MA}) = (K_{MA})_{t=0} e^{-K_H t} \quad (2.8)$$

where K_H is the rate constant of inhibition, and most probably, to some degree dependent on the inhibitor concentration in the water column.

The equations are analogous to the theory of catalyst inhibition or poisoning by Levenspiel [11].

Canadian researchers have identified the coating to be partially clay minerals (Nels Conroy, personal communication). Wetzler *et al.* [12] observed inhibition effects on calcite in acidic minedumps.

The photographs in Figs. 2 and 3 indicate that the calcite surfaces are covered patchwise by the precipitates rather than by a growing film. The observed drastic reduction of the apparent mass transfer coefficient indicates that the precipitates are solids hindering diffusion. This allows us to rephrase

$$(K_{MA}) = K_{MA} e^{-K_H t} \quad (2.9)$$

2.2. The effect of steady state sedimentation

In addition to the inhibition of the calcite surfaces, the steady state sedimentation of particles and organic material will slowly bury any calcite on the bottom.

The sudden neutralization of a lake may also induce short term precipitation of substances such as metal hydroxides.

Dillon *et al.* [10] determined the sedimentation rate for a number of lakes in the Sudbury area to be approximately of the size $1-2 \text{ mm y}^{-1}$.

This implies that the diffusional boundary layer will grow slowly from its initial thickness of the order 10^{-2} m . The observed sedimentation rates will have little effect on the mass transfer coefficient compared to the effect of calcite surface inhibition. However, the available sedimentation rates were determined for clear water lakes, and the rates may be substantially higher in very humic lakes, containing a high concentration of suspended organic material.

The diffusivity in the sediment may be calculated with the Maxwell relation given in Appendix 1.

3. Dissolution of calcite on the lake bottom, taking the inhibition of the particles into account

When we want to take the inhibiting factor into account, we can do this by substituting either eq. (2.7) or eq. (2.8) for $K_M A$ in eqs. (1.8) and (1.7). Most lakes have a steady supply of humic material and aluminium and iron ions from their tributaries, and for this reason we shall make use of the eq. (2.9) and insert it in a mass balance for the lake with the average residence time T . For the hydrogen ion we get

$$\frac{dC}{dt} + \left(1 + \frac{K_M^0 P T}{S} e^{-K_H t}\right) \frac{V^*}{V_L} C = C_{IN} \frac{V^*}{V_L} \quad (3.1)$$

with the boundary condition

$$t = 0 \quad C = C_0 \quad (3.2)$$

For convenience we rewrite eq. (3.2) as

$$\frac{dC}{dt} + (\alpha + \beta e^{-\nu t}) C = \gamma \quad (3.3)$$

where

$$\alpha = \frac{V^*}{V_L}; \quad \beta = \frac{K_M P}{S}; \quad \gamma = C_{IN} \frac{V^*}{V_L}; \quad \nu = K_H \quad (3.4)$$

To solve eq. (3.1) we substitute the variables; assuming $T = V_L/V^*$ to be constant

$$Z = \frac{\beta}{\nu} e^{-\nu t} \quad (3.5)$$

$$dZ = -\nu Z dt \quad (3.6)$$

$$C = \frac{\gamma}{\nu} W \quad (3.7)$$

$$dC = \frac{\gamma}{\nu} dW \quad (3.8)$$

$$n = \frac{\alpha}{\nu} \quad (3.9)$$

which transforms eq. (3.1) to

$$Z \frac{dW}{dZ} = (n + Z)W - 1 \quad (3.10)$$

Equation (3.10) is inhomogeneous but the corresponding homogeneous equation

$$Z \frac{dW}{dZ} = (n + Z)W \quad (3.11)$$

has the general solution

$$W = U Z^n e^Z \quad (3.12)$$

The general solution of eq. (3.10) may now be found by the method of variable constants. Thus we write $U = U(Z)$ and insert this in eq. (3.10)

$$\left(\frac{dU}{dZ}\right) Z^{n+1} e^Z = -1 \quad (3.13)$$

i.e.

$$\frac{dU}{dZ} = -Z^{-(n+1)} e^{-Z} \quad (3.14)$$

Hence

$$U = B + \int_Z^\infty \theta^{-(n+1)} e^{-\theta} d\theta \quad (3.15)$$

and accordingly the solution of eq. (3.10) can be written

$$W = \left(B' + \int_Z^\infty \theta^{-(n+1)} e^{-\theta} d\theta\right) Z^n e^Z \quad (3.16)$$

In this integral infinity was chosen as the upper limit as the integral fails to converge around zero.

In most cases however the concentration load and inlet flow rate will be time variant

$$C_{IN} = C_{IN}(t) = \zeta(Z) \quad V^*/V_L = 1/T = \tau(Z) \quad (3.17)$$

$$C' = C\omega \quad \omega = 1/K_H \quad (3.18)$$

and the general solution of eq. (3.1) can be expressed with the integral

$$C' = B'' - \frac{1}{\omega} \left[\exp \left(Z + \omega \int_Z^\infty \frac{\tau}{Z} dZ \right) \right] \times \left[\int_Z^\infty \frac{\zeta \tau}{Z} \exp \left(- \left(Z + \omega \int_Z^\infty \frac{\tau}{Z} dZ \right) \right) dZ \right] \quad (3.19)$$

3.1. The calcium concentration

The concentration of Ca^{2+} can be calculated as well from a mass balance. If we call the concentration of calcium Ca and that of hydrogen ion C_L we can for the dissolution from the bottom, write

$$-\frac{dM}{dt} = K_M e^{-K_H t} C_L A_L P M_E \quad (3.20)$$

and accordingly the mass balance for a well mixed lake

$$\frac{d\text{Ca}}{dt} + \frac{V^*}{V_L} \text{Ca} = \frac{K_M P T}{S} e^{-K_H t} C_L \frac{V^*}{V_L} + \text{Ca}_{IN} \frac{V^*}{V_L} \quad (3.21)$$

For constant flow and inlet concentrations the integral may be solved analytically.

The amount calcite dissolved can be written as

$$-\frac{dM}{dt} = K_M C_L A_L P M_E e^{-K_H t} \quad (3.22)$$

And the amount dissolved at the time t after liming is given by the integral

$$M - M_0 = K_M A_L M_E \int_0^t P C_L dt \quad (3.23)$$

where C_L is the hydrogen ion concentration in the lake, and K_M the mass transfer coefficient for transport from the sediment surface to the water column.

For cases where the amount of calcite on the bottom is large and the inhibition rapid, a small fraction of the total available mass will dissolve, and accordingly P may be assumed constant.

4. Estimation of the humus inhibition rate

In order to estimate the inhibition rate, an experiment was designed for laboratory measurements. In addition, data from the large data files at the Swedish National Board of Fisheries were analysed to get an estimation from some of the lake limings carried out in Sweden.

4.1. Theory

When there are no tributaries or outlets, the equations can be simplified as follows

$$-\frac{dM}{dt} = K_M C_L A_L P M_E e^{-K_H t} \tag{4.1}$$

for dissolution from the bottom surface.

In the laboratory C_L will be the bulk concentration in the experimental tank. Equation (4.1) can be integrated and for the two different cases of inhibition we get for finite inhibition

$$M - M_0 = C_L M_E A_L \left(\frac{K_M^0 t + \frac{K_M^0 - K_M^\infty}{K_H} (1 - e^{-K_H t}) \right) \tag{4.2}$$

K_M^0 is the initial mass transfer coefficient, and K_M the coefficient at completed deactivation. For infinite deactivation the equation may be simplified to

$$M - M_0 = \frac{K_M^0 A_L M_E C_L}{K_H} (1 - e^{-K_H t}) \tag{4.3}$$

4.2. Experiment

The inhibition rates were studied in an apparatus as shown in Fig. 4. This cell was connected to a pH-stat apparatus which kept the pH-value constant and which recorded the acid supplied for dissolution.

The sand bed in the cell was covered with a layer of calcite to make a porous surface, similar to what could be envisioned to exist on a lake sand bottom. Later this layer was, in addition, covered with sand or sediments to test if the Maxwell relation

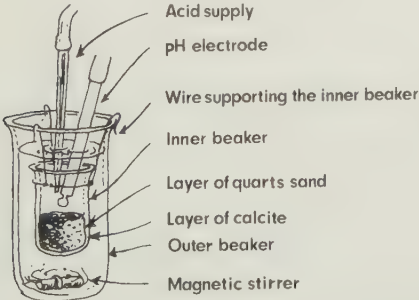


Fig. 4. The cell used for measurement of diffusion in heterogeneous media, and for measurement of the inhibition rate. The cell shown was connected to a pH-stat, and the addition of acid measured.

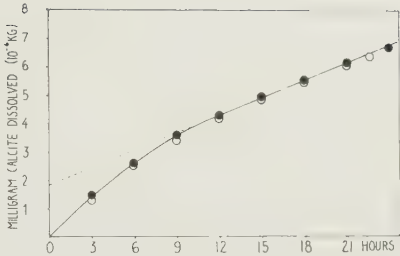


Fig. 5. Amount calcite dissolved in two deactivation experiments. From the intercept at $t = 0$ an estimate of the deactivation rate may be made.

was holding for this type of systems (see Appendix) [13]. As the cell was operated under conditions far from calcite saturation concentration, eq. (4.2) was used to estimate K_H .

Some of the results are shown in the Figs. 5 and 6 where water from the lake Tjurken was used. Some of the chemical data for this water is given in Table II. The water is typical of very many Swedish forest brown water lakes. The curves can be seen to follow the theory well. From the intercept in Fig. 5, an estimate of the inhibition rate can be derived

$$K_H = 1.8 \times 10^{-5} \pm 0.3 \times 10^{-5} \text{ s}^{-1}$$

This value implies that the calcite will be deactivated within 15–30 hours after being deposited on the bottom, in extreme brown waters as the water used in the experiment.

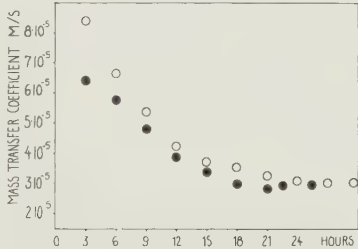


Fig. 6. The observed mass transfer coefficient in two deactivation experiments.

Table II. Composition of the water used in the laboratory experiment to determine the inhibition rate

pH	4.60
Alkalinity	—
Ca	0.190 meqv/l
Mg	0.105 meqv/l
Na	0.223 meqv/l
K	0.026 meqv/l
Al	0.2 mg/l
Fe	1.0 mg/l
Si	3.0 mg/l
SO ₄ ²⁻	0.356 meqv/l
DOC-Mn	66.8 mg/l
Colour	100 mg Pt/l

4.3 Estimation from lake liming data

If little of the calcite dissolves directly, the larger part settles on the bottom in a like liming. Then the alkalinity and pH-values will gradually rise to a maximum value. By using eq. (3.1) we

can, for this hydrogen ion concentration minimum, C_{MIN} , write

$$\frac{dC}{dt} = 0 \quad (4.4)$$

$$K_H = -\frac{1}{t_M} \ln \left(\frac{(C_{\text{IN}} - C_{\text{MIN}})S}{K_M PTC_{\text{MIN}}} \right) \quad (4.5)$$

where t_M is the time from the liming to the minimum. However, this estimate is rather indeterminate as the pH-value is not conservative and may be influenced by many other factors. An estimate can be derived separately from the calcium concentration curve, using equation

$$\frac{dC_a}{dt} + \frac{1}{T} C_a = \frac{1}{T} C_{a\text{IN}} + \frac{K_M^0 P}{S} e^{-K_H t} C_L \quad (4.6)$$

to obtain

$$K_H = -\frac{1}{t_M} \ln \left(\frac{\left(\frac{dC}{dt} T + (C_{a\text{MAX}} - C_{a\text{IN}}) S \right)}{K_M^0 PTC_L(t_M)} \right) \quad (4.7)$$

There are two cases that must be distinguished; in the first, the calcium concentration will slowly rise from $C_{a\text{IN}}$ to a maximum $C_{a\text{MAX}}$, in which case $dC/dt = 0$ and t_M is the time needed to reach the maximum. $C_L(t_M)$ will be the hydrogen ion concentration at t_M . In the other case the concentration will decay from an initial level established by the liming of the lake, and the maximum is obtained as the point of maximum difference between exponential decay and the actual concentration curve.

This estimation procedure does, however, only give a minimum limit for the value of K_H . The model assumes the lake to resemble an ideally stirred tank, which is not quite true. The lake is far from ideally mixed. It has zones with holdbacks and it stratifies during the summer. All these effects influence the value observed for K_H of which some of the estimates are listed in Table III together with the water colour value. This estimate is also dependent on a rather accurate estimate of the mass transfer coefficient K_M , and the accuracy is estimated to $\pm 2/3 K_M$. If a mass balance can be made, K_H may also be estimated from a plot of $\ln(dM/dt)$ vs. t , using:

$$-\frac{dM}{dt} = K_M^0 C_L A_L P M_E e^{-K_H t} \quad (4.1)$$

or

$$\ln \left(-\frac{dM}{dt} \right) = -K_H t + \ln(K_M^0 C_L A_L P M_E) \quad (4.8)$$

This method gives an estimate independent of the other variables and is accordingly more reliable. There is, however, a limited amount of data sets that permits this equation to be used [18].

It would seem reasonable to try to relate the inhibition rate to the contents of aluminium or iron in the water, but at present there are not enough data available to do this properly.

4.4. The mass transfer coefficient, K_M

The mass transfer from the sediment will be determined by the eddy diffusion in the boundary layer above the bottom. This was estimated from the diagram in Fig. 7. This figure relates the eddy diffusion to the thickness of the hydrodynamic boundary layer. The cross marks the value successfully used in another model for the diffusion of chemicals out of sediments [5, 14-17, 19-22]. This value was also used in this study.

Table III. A list of estimates for the inhibition rate from lake liming data. The values given are approximated using eqs. (50), (52) or (53). The lake liming data were obtained from the Swedish National Fisheries Board in Göteborg. For waters with a colour value less than 50 mg Pt/l, the inhibition rate had an average value of $K_H = 1.8 \pm 1.0 \text{ yr}^{-1}$

Lake	K_H			Water colour mg Pt/l
	Eq. (53)	Eq. (52)	$\tilde{K}_H$	
Övre Bolsjön	0.40-0.80	0.20-1.10	0.63	15-35
Södra Blötevatten	0.32-1.18	0.14-0.76	0.50	5-20
Norra Blötevatten	0.63-0.98	0.15-0.80	0.64	15-20
Eigdesjön	0.18-1.40	0.10-0.58	0.56	5-10
Sörvamsjön	0.18-1.40	0.30-1.70	0.90	5-25
Nordvamsjön	0.61-1.24	0.50-2.81	1.30	10-20
Ekelidvattnet	0.44-0.76	0.32-1.82	0.84	20-45
Bredvatten	0.60-1.40	0.36-2.02	1.10	5-10
Lysevatten	1.30-2.20	0.40-3.20	1.78	7-15
Ski Tjärn	0.14-0.68	0.32-1.79	0.73	5-10
Stensjön	-	0.64-3.65	2.15	20-40
Trehörningen	-	0.22-1.30	0.75	25-50
Vällsjön	-	0.71-4.0	2.35	3-5
Långtjärn	-	0.43-2.6	1.50	7-15
Blomman	-	0.08-0.44	0.26	5-10
Hornasjön	-	0.51-2.90	1.70	3-5
Lilla Härsjön	-	0.80-4.80	2.65	3-5
Kullsjön	-	0.20-1.1	0.65	5-10

Mean value 1.17 yr^{-1} (± 0.58)

Soil/brook liming

Finspångs revir	100-500	320	150-500
Soil liming 1*	0.40-2.0	1.22	-
Soil liming 2*	0.18-1.0	0.59	-
Soil liming 3*	0.50-2.50	1.50	-
Abborbäcken, Anråseån	1.0-5.9	3.50	20-50
Säggvarnsbäcken	0.3-1.7	1.00	-
Västra Skälsjöbäcken	2.9-16.0	9.50	-
Trehörningen, Marsh	300-1300	790	200-300
Borås, Limed Brook	20-900	70	100-200

* Report 4:81 from the Swedish Freshwater Institute.

4.5. The P factor

P is the fraction of the lake bottom area that can be considered to be all calcite surface. It will depend on the grain size of the calcite, and may be estimated from Fig. 9 showing the particle size distribution of several calcite powders, and their area covering capability as regards amount per hectare in Fig. 8.

P was calculated using the expression:

$$P = M_0^{1/3} M_0^{2/3} \frac{3\Phi_K}{4\rho} \sum_i \frac{\Delta\phi_i}{r_i} \quad (4.9)$$

where M_0 is the amount spread and A_L the total lake area. P is then the fraction of A_L totally covered with calcite.

4.6. The reacidification of Övre Bolsjön, Bredvatten and Lysevatten

Calculations have been made for two lakes near Göteborg which were limed in 1974 with T-chalk, a calcium-silicate which in terms of dissolution behaves much like calcite. The lakes have been monitored since then by Hans Hultberg at the IVL in Göteborg. Bredvatten was relimed in 1979, Lysevatten has reacidified completely. Both Bredvatten and Lysevatten was limed in the littoral zone of lakes. Övre Bolsjön was limed in

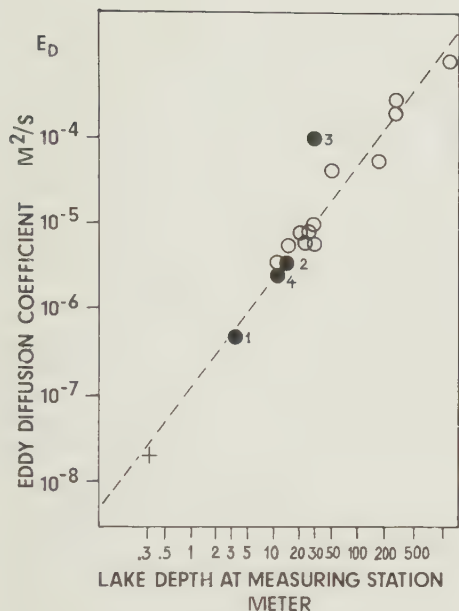


Fig. 7. The overall transport of mass from the bottom to the bulk of the lake, is much determined by the eddy diffusivity in the water column above the sediments. The points in the figure are partially taken from Mortimer [17]. The black dots represent estimates from the build up of chemical gradients during summer stratification after the lakes were limed. The lakes are: 1, Tjurken; 2, Ölen; 3, Barken; and a lake which had its sediments treated with soda: 4, Lilla Galtsjön. The cross represents the value used in the computer model for Lilla Galtsjön by Warfvinge and Sverdrup [5].

1976 with 500 tons of calcite powder no 6, called 0–0.5 mm, all in the lake, mostly in the littoral zone. The physical characteristics of the lakes and the liming performed are listed in Tables IV and V.

The actual tributary flow rate was known for Övre Bolsjön, and an integrated mass balance for calcium could be made for the period 1976–1980. For Bredvatten and Lysevatten mass

balances are available from Hans, Hultberg's report to the Swedish National Board of Fisheries 1979 [23].

The computer calculations for the three lakes are shown together with the observed values in Figs. 13, 14 and 15, for pH, alkalinity and calcium concentrations. It can be seen that the model describes the reacidification fairly well. The actual mass-balances are compared to the calculations in Figs. 16 and 17, to control the reliability of the model, as well as Fig. 17 where the predictions are plotted vs. the observations.

The inhibition rate coefficient was set at the value 0.8 y^{-1} for the calculations on Bredvatten and Lysevatten, and at 0.7 y^{-1} for Övre Bolsjön. This is a good agreement with the values estimated in Table III.

4.7. Modelling lakes in series

The model was tested on the Vammsjön–Blötevatten lake system with five lakes in series. All the lakes were limed with T-Chalk late in 1974. The calculated values can be seen together with the observations in Figs. 19 and 20.

4.8. Calculation of the reacidification process

A computer code was written to calculate the reacidification of a limed lake with calcite on the bottom. It was written for a small desk computer, in order to be very easy to use and with a high availability. A schematic view of the model is given in Fig. 10, each lake in a series modelled as a tank. A more complicated model like the one shown in Fig. 11 was also tried. It considers both the stratification and the spring and autumn turnovers. However, it was felt that the large increase in indata necessary did justify the small improvement in result. Alas only the simpler model will be used here.

The model will need as indata:

- Initial pH in the lake after liming
- Annual average pH in the tributary
- Initial calcium concentration after liming
- Annual mean calcium concentration in the tributary
- Mean lake depth
- Mean residence time
- Lake volume
- The total amount of calcite on the bottom
- Fraction of the total amount of calcite, on the bottom
- Inhibition coefficient

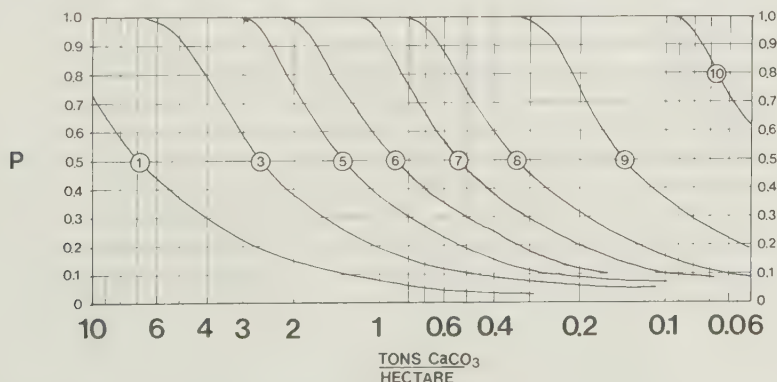


Fig. 8. Calcite powders with different particle size distributions have different ability to cover the area on which it is resting. Therefore the dosage of powder and the particle size distribution must be known to

predict the parameter P . Usually a dosage of $15\text{--}30 \text{ g m}^{-2}$ are applied to lakes when No. 7 is used. This is equivalent to $0.5\text{--}1.0 \text{ ton CaCO}_3$ per hectare. The powders are defined in Fig. 6.

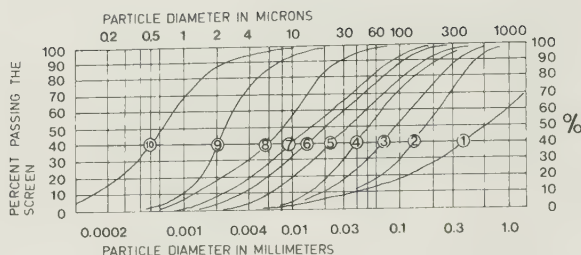


Fig. 9. Partial size distribution of calcite powders tried in liming projects in Sweden. The powders 6 and 7 are the most commonly used and classified commercially as 6, 0–0.5 mm; 7, 0–0.2 mm.

and for lakes in series

Fraction of the tributary flow from upstream lake.

The model will calculate pH, alkalinity and calcium as well as the amount calcite dissolved.

As the intention with this model is to make predictions, are the annual tributary flow variations parameterized for the coastal, inland and mountain regions of Sweden, based on statistical data from long term measurements. The variations

used are shown in Fig. 12, where No. 1 represents the coastal regions, No. 2 inland regions and No. 3 mountain regions.

4.9. Reacidification of limed lakes

The model may be used to calculate the reacidification rate for lakes in general.

Several runs were made, taking as an example a lake with volume of $1.5 \times 10^6 \text{ m}^3$, mean depth 5 m, that was assumed to start at pH 7.0 with 50% of the calcite amount added on the bottom, and tested with different average residence times.

Table IV. Physical characteristics of the lakes to which the dissolution/inhibition model was applied

Lake no.	Volume mill. m ³	Retention years	Mean depth meter	Maximum depth meter	Fraction of tributary from upstream lake %	Lake area as percent of the total watershed area %
<i>Lakes in series</i>						
Söndra Blötevatten	1	1.17	2.6	8.1	27	13.0
Nordra Blötevatten	2	0.51	0.7	5.4	18	5.2
Eigdesjön	3	5.27	2.9	6.3	28	18.0
Sörvamsjön	4	4.59	1.25	8.3	27	5.7
Nordvamsjön	5	0.62	0.14	4.8	13	1.1
<i>Single lakes</i>						
Övre Bolsjön	17.56	4.6	12.6	20		14.6
Bredvatten	0.92	2.4	3.4	7		31
Lysevatten	1.91	3.7	4.7	17		33

Table V. Chemical data for the lakes to which the dissolution/inhibition model was applied. The tributary pH is the annual average pH value for the tributaries before liming. The date given is the date of liming

	Before liming			After liming				Dosage neutralizing agent g/m ³	Neutralizing agent	Date	No.
	Tributary	Epilimnion		Epilimnion		Hypolimnion					
	pH	pH	Ca ²⁺	pH	Ca ²⁺	pH	Ca ²⁺				
<i>Lakes in series</i>											
Söndra Blötevatten	4.85	4.70	1.8	7.30	5.4	—	—	26	0–0.5 mm T-Chalk	3/74	1
Nordra Blötevatten	4.60	4.50	1.8	7.10	5.8	—	—	20	0–0.5 mm T-Chalk	4/74	2
Eigdesjön	4.95	4.70	2.1	6.90	5.7	—	—	13	0–0.5 mm T-Chalk	5/74	3
Nordvamsjön	5.20	5.20	2.0	7.00	6.6	10.00	—	20	0–0.5 mm T-Chalk	1/75	4
Sörvamsjön	5.00	5.00	2.1	6.80	7.9	7.60	—	10	0–0.5 mm T-Chalk	2/75	5
<i>Single lakes</i>											
Övre Bolsjön	5.20	5.20	2.4	7.20	6.8	7.70	9.6	29	0–0.5 mm Calcite	5/76	
Bredvatten	4.90	4.50	1.5	7.30	7.6	7.30	7.6	44	0–0.5 mm T-Chalk	5/74	
Lysevatten	4.95	4.60	1.8	7.40	7.5	5.00	2.2	32	0–0.5 mm T-Chalk	5/74	

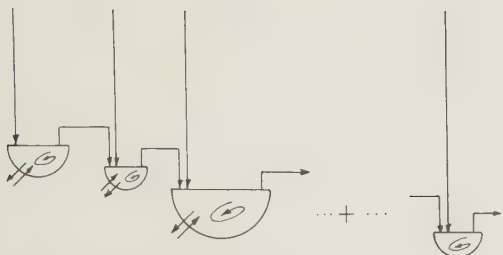


Fig. 10. In the model each lake is viewed as a stirred tank.

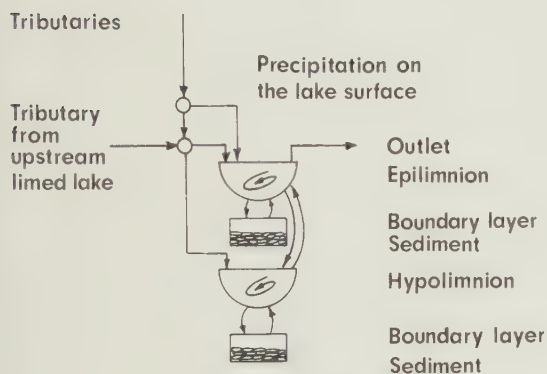


Fig. 11. A more complicated model was also tested, but gave few advantages, and little improved accuracy in relation to the increased amount of indata needed.

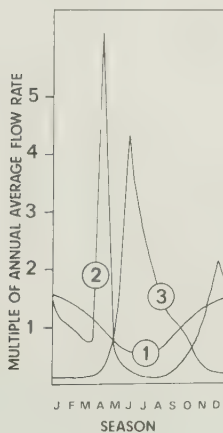


Fig. 12. The annual tributary flow variations were classified as one of three types depending on the location. No. 1 is taken as typical for coastal regions, No. 2 as typical for inland regions, and No. 3 as typical for mountainous regions.

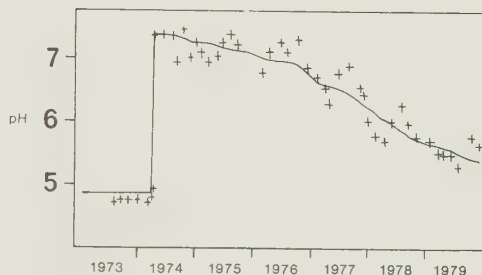
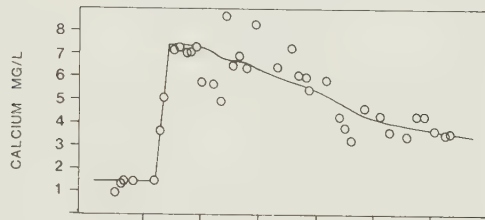
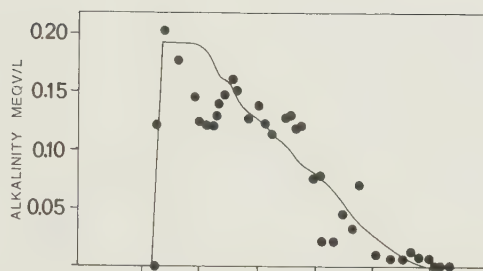


Fig. 13. Calculated and observed reacidification for lake Bredvatten.

The duration of the liming result until pH 6.0 can be plotted versus the mean residence time for the lake to produce the curve in Fig. 21. The estimated duration of the result for several Swedish lake limings are included as well. Their volumes vary in the range $0.46 \times 10^6 \text{ m}^3$ – $17.5 \times 10^6 \text{ m}^3$ and the average depth vary from 3 m to 12.5 m, as well as the fraction of the total amount of calcite added, on the bottom vary from 30% to nearly 80%.

For lakes with a residence time shorter than half a year will the result be very sensitive to sudden depressions in the pH-value in the tributaries that may occur during snow melt or autumn rains. In such cases neutralization may be achieved with methods for liming running waters.

5. Discussion

The model presented in this study is a simple model in which the inhibition concept takes care of more than one mechanism affecting the long term dissolution of calcite. It lumps together the combined effects of dispersion, sedimentation, sorption to the sediments and true inhibition.

The reversible sorption of calcium to the sediments play an important role in determining the mass balance for calcium, and the amount of it available to the water column. Organic

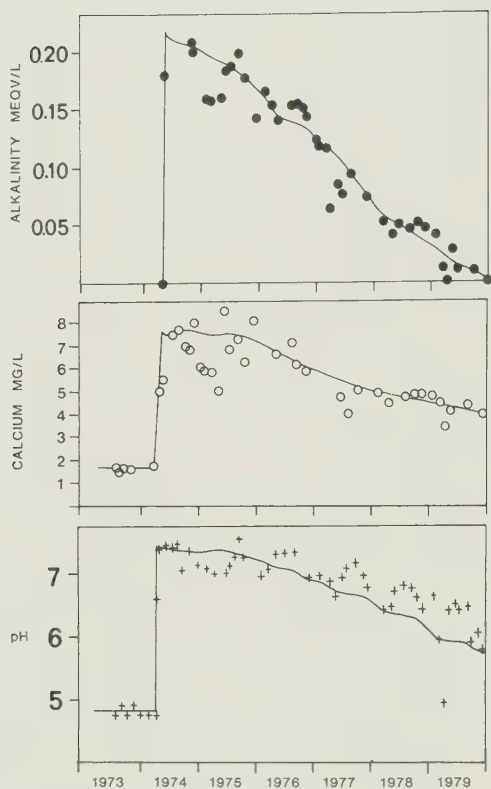


Fig. 14. Calculated and observed reacidification for lake Lysevatten.

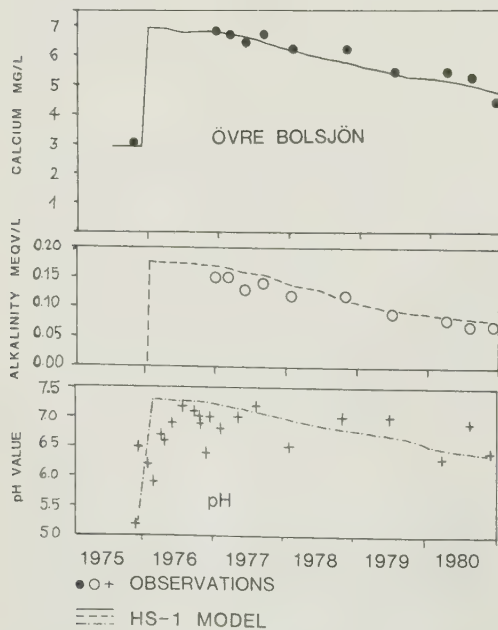


Fig. 15. Calculated and observed reacidification for lake Övre Bolsjön.

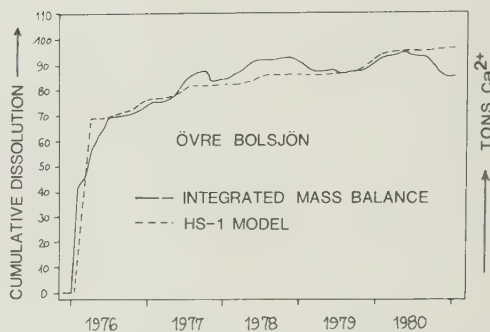


Fig. 16. The observed integrated mass balance as compared to the calculated (-----) for lake Övre Bolsjön. The lake was limed in 1976 with 500 tons of calcite powder No. 6 classified as 0–0.5 mm. Approximately 38% dissolved at once after liming, and another 10% later on.

sediments may consume considerable amounts of calcium or magnesium from the water column.

Models for the sorption of calcium to the sediments are being incorporated into the reacidification model.

Acknowledgement

Bo Bengtsson at the Swedish National Board of Fisheries Göteborg, helped a great deal by giving access to the large liming data files kept there.

Hans Hultberg of the IVL supplied accurate data from the lakes Bredvatten and Lysevatten.

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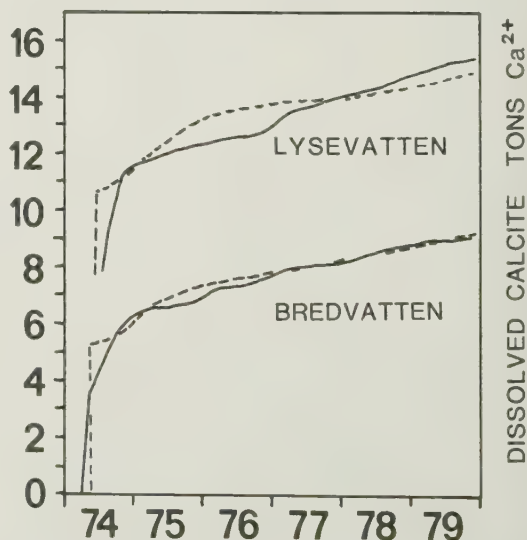


Fig. 17. The calculated mass balances for lake Bredvatten and Lysevatten (-----) as compared to the mass balances given by Andersson and Hultberg (1979) (——).

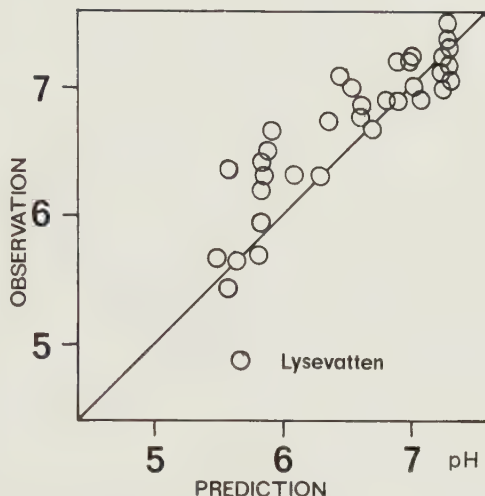
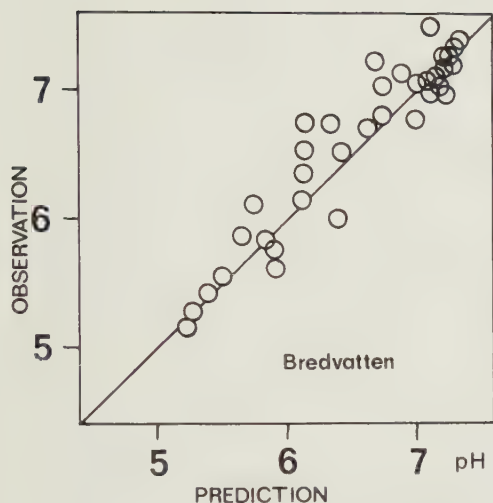


Fig. 18. The observed pH-values as compared to the predictions made with the model for lake Bredvatten and lake Lysevatten.

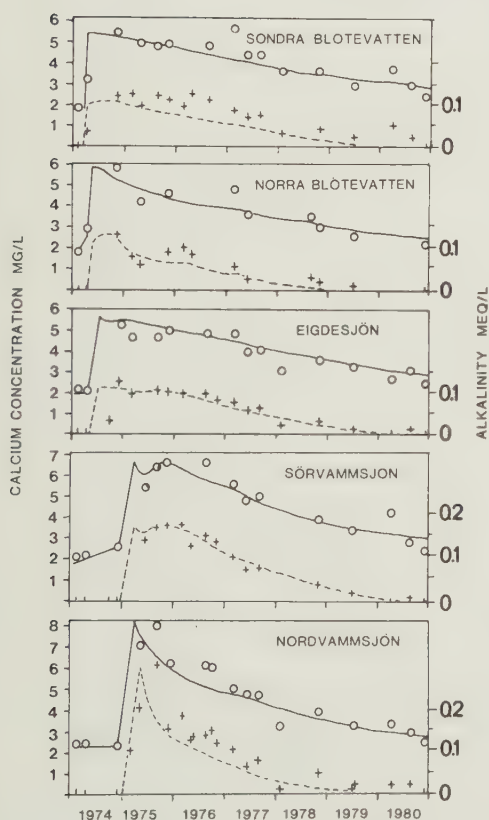


Fig. 19. A calculation run for 5 lakes in series in the Vammsjön-Blötevatten lake system. All the 5 lakes were limed in late 1974 with T-Chalk. The diagrams show the calculated calcium concentrations (—) and alkalinity (-----) together with the observed values. The deactivation rate was set at 0.6 y^{-1} .

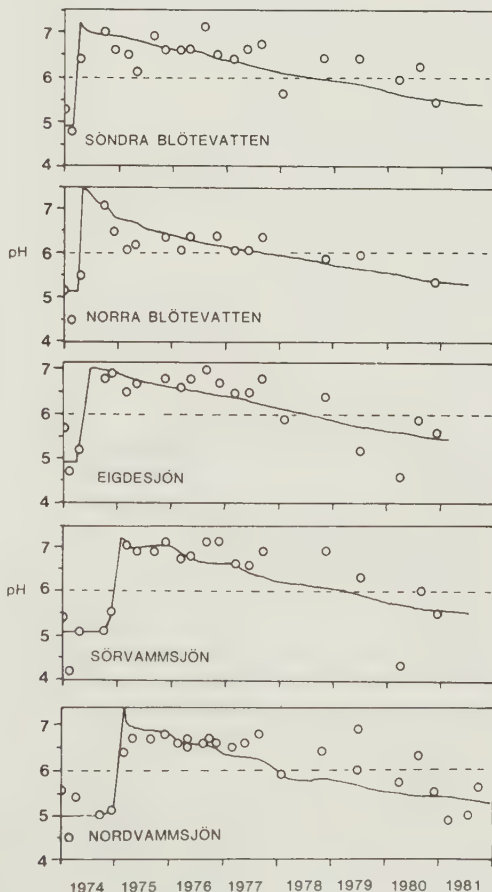


Fig. 20. The predicted pH-value (—) as compared to the observations (o) in the Vammsjön-Blötevatten lake system.

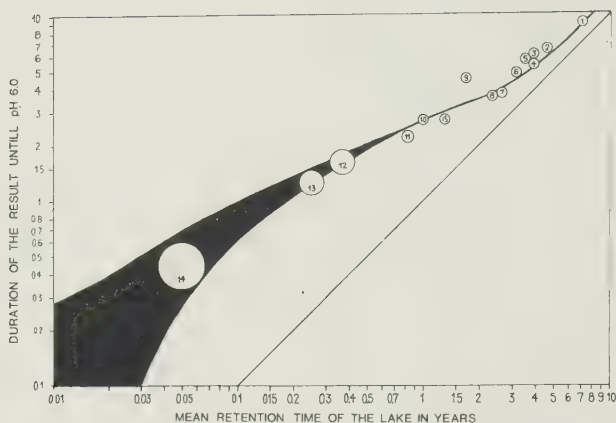


Fig. 21. The time required for a lake to reacidity from pH 7 to pH 6 was calculated for a lake with a volume of 1.5 million m^3 and mean depth 5 m, with different residence times. The circles are observations from limed lakes: 1, Hornasjön, Göteborg; 2, Övre Bolsjön, Bohuslän; 3, Lysevatten, Göteborg; 4, Smedvatten, Göteborg; 5, Ski tjärn, Värmland; 6, Blomman, Göteborg; 7, Söndra Blötevatten, Bohuslän; 8, Bredvatten, Göteborg; 9, Stensjön, Värmland; 10, Grytsjön, Örebro; 11, Ekelid-

vattnet, Bohuslän; 12, Nedre Särnamannasjön, Jämtland; 13, Tarmälången, (Report from the Freshwater Inst.); 14, Kälåbodasjön, Småland; 15, Jällunden, Halland. The lake volume varied from 17 mil. m^3 to 0.4 mil. m^3 and the mean depth varied from 15 m to 2 m in the observed lakes. For residence times shorter than 0.5 years will the lake be very sensitive to sudden pH depressions in the tributaries that often occur at high flow rates in acidified regions.

Appendix I

When diffusion takes place through sediment

The diffusion through sediment is a process going on in a heterogenous media. For the diffusion coefficient Crank [13] gives the relation where y is the fraction of solids

$$\frac{D - D_L}{D + aD_L} = Y \frac{D_S - D_L}{D_S + aD_L} \quad (A.1.1)$$

Here D_L is the coefficient for pure water and D_S the coefficient for the pure second phase, in our case stone, and therefore equal to zero. We get for the diffusion coefficient

$$D = D_L \left(\frac{a - aY}{a + Y} \right) \quad (A.1.2)$$

For spheres a equals two, but for objects of other arbitrary forms Crank [13] refers to the empirical expression, where

Φ_K is the sphericity

$$a + 1 = \Phi_K \quad (A.1.3)$$

giving the expression

$$D = D_L \left(1 - \frac{3Y}{3 - \Phi_K - Y\Phi_K} \right) \quad (A.1.4)$$

The sphericity of the sand used in the experiment lies in the range 0.55–0.85 D/D_L is plotted vs. Y for the values used in the experiment in Fig. A.1.

In sediments, Y has an average value of 0.7 and varies from 0.5 to 0.85. Quartz sand used in later experiments had a Y value of 0.5. Typical for marine sediments are $Y = 0.70$ –0.80 in the deeper layers, and $Y = 0.30$ –0.10 in the upper layers. Figure A.2 shows the results of a test made with the apparatus for measuring K_H where K_M^0 is plotted vs sediment thickness.

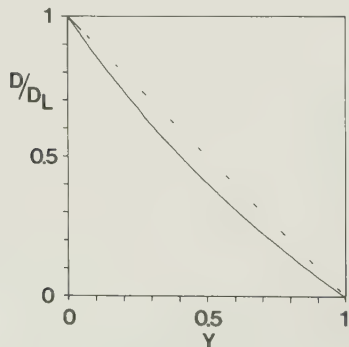


Fig. A.1. The actual bulk diffusivity of the heterogeneous phase plotted vs. the fraction of the volume which is occupied by solids. $\Phi_K = 0.65$ –0.85.

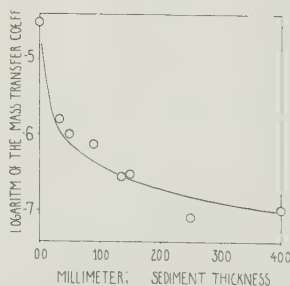


Fig. A.2. The value of the mass transfer through a layer of sand was measured with the cell used to estimate the inhibition rate. The mass transfer coefficient was calculated as $K_M = D^*/X_s$ where X_s is the thickness of the sand layer, and D^* the diffusivity calculated with the Maxwell equation. The drawn line is the theoretical prediction, the circles are observations.

Appendix 2

Development of the analytical solution into rapidly converging series

Equation (38) is the general solution of eq. (32) and accordingly of eq. (23). But as eq. (38) is quite unsuitable for numerical calculations, it is necessary to expand the integral

$$\int_Z^\infty \theta^{-(n+1)} e^{-\theta} d\theta \quad (\text{A.2.1})$$

into rapidly converging series of Z . Equation (A.2.1) can be integrated by parts

$$\int_Z^\infty \theta^{-(n+1)} e^{-\theta} d\theta = \frac{Z^{-n} e^{-Z}}{n} - \frac{1}{n} \int_Z^\infty \theta^{-n} e^{-\theta} d\theta \quad (\text{A.2.2})$$

and this can be repeated

$$\begin{aligned} \int_Z^\infty \theta^{-(n+1)} e^{-\theta} d\theta &= \\ &= Z^{-n} e^{-Z} \left(\frac{1}{n} \frac{Z}{n(n-1)} + \dots + (-1)^\mu \right. \\ &\quad \times \left. \frac{Z^\mu}{n(n-1) \dots (n-\mu)} \right) + \frac{1}{(-n)(-n+1) \dots (-n+\mu)} \\ &\quad \times \int_Z^\infty \theta^{\mu-n} e^{-\theta} d\theta \end{aligned} \quad (\text{A.2.3})$$

Now if $\mu - n > 0$ it can be written for the remainder term

$$\begin{aligned} \frac{1}{(-n)(-n+1) \dots (-n+\mu)} \int_Z^\infty \theta^{\mu-n} e^{-\theta} d\theta &= \\ = \frac{\Gamma(-n)}{\Gamma(\mu-n+1)} \left(\int_0^\infty \theta^{\mu-n} e^{-\theta} d\theta - \int_0^Z \theta^{\mu-n} e^{-\theta} d\theta \right) \end{aligned} \quad (\text{A.2.4})$$

and remember that by definition, we have

$$\int_0^\infty \theta^{\mu-n} e^{-\theta} d\theta \equiv \Gamma(\mu-n+1) \quad (\text{A.2.5})$$

It can be shown that the second term on the right side of eq. (A.2.4) tends to zero as μ increases.

We can write

$$0 < \int_0^Z \theta^{\mu-n} e^{-\theta} d\theta < \int_0^Z \theta^{\mu-n} d\theta = \frac{Z^{\mu-n+1}}{\mu-n+1} \quad (\text{A.2.6})$$

and it is obvious that

$$\lim_{\mu \rightarrow \infty} \frac{\Gamma(-n)}{\Gamma(\mu-n+1)} \frac{Z^{\mu-n+1}}{(\mu-n+1)} = 0 \quad (\text{A.2.7})$$

and

$$\begin{aligned} \int_Z^\infty \theta^{-(n+1)} e^{-\theta} d\theta &= \Gamma(-n) + Z^{-n} e^{-Z} \\ &\quad \times \sum_{\mu=0}^{\infty} (-1)^\mu \frac{Z^\mu}{n(n-1) \dots (n-\mu)} \end{aligned} \quad (\text{A.2.8})$$

and accordingly eq. (3.16) becomes

$$W = B^* Z^n e^Z + \sum_{\mu=0}^{\infty} (-1)^\mu \frac{Z^\mu}{n(n-1) \dots (n-\mu)} \quad (\text{A.2.9})$$

where

$$B^* = B + \Gamma(-n) \quad (\text{A.2.10})$$

Equation (A.2.9) is valid for all values of n except zero and

positive integers. In the case that n should be a positive integer or zero, as may happen, we write

$$\begin{aligned} Z^n e^Z \int_Z^\infty \theta^{-(n+1)} e^{-\theta} d\theta &= \Gamma(-n) Z^n e^{-Z} + \\ &+ \sum_{\mu=0}^{\infty} (-1)^\mu \frac{Z^\mu}{n(n-1) \dots (n-\mu)} \end{aligned} \quad (\text{A.2.11})$$

where $n = N + \epsilon$, and ϵ is a very small number and accordingly

$$\begin{aligned} Z^N e^Z \int_Z^\infty \theta^{-(N+1)} e^{-\theta} d\theta &= \\ = \lim_{\epsilon \rightarrow 0} \Gamma(-n) Z^n e^Z + \sum_{\mu=0}^{\infty} (-1)^\mu \frac{Z^\mu}{n(n-1) \dots (n-\mu)} \end{aligned} \quad (\text{A.2.12})$$

This leads to

$$\begin{aligned} Z^N e^Z \int_Z^\infty \theta^{-(N+1)} e^{-\theta} d\theta &= \\ = \sum_{\mu=0}^{N-1} (-1)^\mu \frac{Z^\mu}{n(n-1) \dots (n-\mu)} + (-1)^N \frac{Z^N}{N!} \times \\ \times \sum_{\mu=0}^{\infty} (-\gamma + \psi(\mu) - \ln Z) \frac{Z^\mu}{\mu!} \end{aligned} \quad (\text{A.2.13})$$

where $\nu = (0.57721 \dots)$ is Euler's constant and

$$\psi(\mu) = 1 + 1/2 + 1/3 + \dots + 1/\mu \quad (\text{A.2.14})$$

The general solution becomes for $n = 1, 2, \dots, n$

$$\begin{aligned} W &= BZ^n e^Z + \sum_{\mu=0}^{n-1} (-1)^\mu \frac{Z^\mu}{n(n-1) \dots (n-\mu)} + \\ &+ (-1)^n \left(\frac{Z^n}{n!} \right) \sum_{\mu=0}^{\infty} (-\nu + \psi(\mu) - \ln Z) \frac{Z^\mu}{\mu!} \end{aligned} \quad (\text{A.2.15})$$

With eqs. (A.2.9) and (A.2.15) the concentration of H^+ can be computed as a function of time for any lake system with constant inlet acidification load.

List of symbols

A	Surface area	(m ²)
A_L	Surface area of the lake bottom	(m ²)
$B, B', \dots$	Integration constants	
C	Concentration	(kmol m ⁻³)
C_{in}	Concentration in the tributary	(kmol m ⁻³)
Ca	Calcium concentration in the lake	(kmol m ⁻³)
C_L	Concentration in the lake volume	(kmol m ⁻³)
C_1	Substitution constant	
C_0	Initial concentration	(kmol m ⁻³)
D	Diffusivity	(m ² s ⁻¹)
D_L	Diffusivity in the liquid phase	(m ² s ⁻¹)
D_S	Diffusivity in the solid phase	(m ² s ⁻¹)
I	Amount of inhibitor	(kg)
$k_1, k_2, \dots$	Reaction rate coefficients	
K_p	Precipitation rate coefficient	(kg m ⁻² s ⁻¹)
K_D	Deactivation rate coefficient	(m ² kg ⁻¹)
K_M	Mass transfer coefficient	(m s ⁻¹)
K_H	Inhibition rate constant	(y ⁻¹)
M	Mass	(kg)
M_0	Initial mass	(kg)
M_E	Equivalent mass for neutralization	(kmol kg ⁻¹)
P	Fraction of the bottom covered	
r	Radius	(m)

R	Reaction rate	($\text{kmol m}^{-2} \text{s}^{-1}$)
S	Mean lake depth	(m)
t	Time	(yr)
T	Mean residence time	(yr)
U	Particular integral of dissolution integral	
V_L	Lake volume	(m^3)
V^*	Tributary flow rate	($\text{m}^3 \text{s}^{-1}$)
X_s	Boundary layer thickness	(m)
W	Concentration transform	
X	Distance	(m)
Y	Volume fraction of solids	
Z	Inhibition transform function	
Γ	Gamma function	
ϵ	Limes variable	
Φ_K	sphericity	
π	3.14...	
$\alpha \beta \gamma$	Transform symbols	
$\eta \lambda \omega$		
$\nu \mu \Phi$		
$\theta \beta_i \gamma_i$		
$\zeta(Z)$		Transform function
$\tau(Z)$	Transform function	
$\rho(Z)$	Transform function	

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A Reacidification Model for Acidified Lakes Neutralized With Calcite

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In lake liming operations in Sweden, acidified lakes are reclaimed by neutralization with calcite powder. The amount added is intended to neutralize the water column as well as to delay the reacidification. The reacidification of limed lakes is dependent on the dilution of the dissolved calcium carbonate with time and, for a limited period of time, the dissolution of calcite from the lake sediments. Calcite on the lake bottom will, in addition to being covered by sedimentation, become inactivated by precipitates of humus and clay minerals clogging the calcite surfaces. A model has been developed to calculate the reacidification of a limed lake which includes the following mechanisms: (1) the dissolution of calcite and a subsequent neutralization of acid water, (2) owing to the increase in pH value, occurrence of precipitation of humus and dissolved metals onto the calcite surface and inhibition of the dissolution of calcite (3) reversible sorption of calcium from the water column by sediments not covered with calcite, and (4) diffusive transport through a boundary bottom layer to the water column. In a first approach the lake was modeled as a continuously stirred tank. The equations were derived from a mass balance and the dissolution kinetics for calcite to describe the long-term development of pH, alkalinity, and calcium concentration in the lake. The differential equations describing the mechanisms were solved with the help of a computer code. The model accurately describes the reacidification and the mass balances observed in several limed lakes.

INTRODUCTION

Thousands of lakes and rivers in Scandinavia and North America located on low weathering bedrock or surrounded by soils with a low calcite content are suffering from the effects of acid rain. In Norway and Sweden waters in the southern parts of the countries, an area of almost 200,000 km², will have critical pH values during some time of the year. Nearly 40,000 lakes are affected in addition to countless kilometers of rivers and brooks.

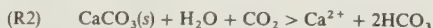
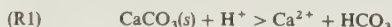
The measure most frequently taken is liming of the river or lake affected. This is in fact the only large-scale remedy available until emissions of SO₂ and NO_x have been reduced drastically on the European continent. In Sweden, large programs for liming of lakes and running waters are in progress and about \$20,000,000 (U.S.) will be spent each year in the final program. It is quite obvious that it is of great importance to use the resources as efficiently as possible.

Acidified lakes in Sweden are reclaimed by distributing calcite powder in the lakes. This neutralizes the acid and restores the alkalinity. A large fraction of the calcite dissolves during sinking, and the rest precipitates on the bottom. This study concerns the dissolution of calcite from the bottom and the modeling the process of reacidification.

In earlier works we have studied several aspects of liming, such as the dissolution of calcite in acidic solution [Sverdrup and Bjerle, 1982], calcite dissolution and lake liming [Sverdrup and Bjerle, 1983; Sverdrup, 1983a, b; Warfvinge et al., 1984], the transport of substances from the sediments in lakes [Warfvinge et al., 1983], liming of running waters [Sverdrup et al., 1984a], a simple model for the reacidification of limed lakes [Sverdrup et al., 1983, 1984b; Sverdrup and Warfvinge, 1984a], integrated mass balances for limed lakes [Sverdrup and Warfvinge, 1984b], and soil liming [Warfvinge and Sverdrup, 1983]. One earlier attempt to make a reacidification model is known to us [Dillon, 1984]. However, this model did not take any reaction with residual calcite or any sediment-water interaction into account and therefore failed to simulate the observed results.

DISSOLUTION OF CALCITE IN LAKES

The dissolution of calcite in dilute acidic aqueous solution can be described as a heterogeneous solid-liquid reaction controlled by diffusion. The chemical reactions involved are



In natural waters with pH values below 5.5 and a carbon dioxide partial pressure less than 0.3 atm, (R1) will dominate, and the dissolution rate will be proportional to the hydrogen ion concentration, while at higher pH values, (R3) will dominate. If the carbon dioxide partial pressure exceeds 0.3 atm, (R2) will contribute to the dissolution rate, and it may be increased as much as one order of magnitude [Bjerle et al., 1982].

The backward reaction rate can be shown to be dependent on the hydrogen bicarbonate concentration, and the dissolution rate may be described with the general expression [Plummer et al., 1978]

$$R = k_1(\text{H}^+) + k_2(\text{CO}_2) + k_3(\text{H}_2\text{O}) + k_B(\text{Ca}^{2+})(\text{HCO}_3^-) \quad (\text{kmol/m}^2\text{s}) \quad (1)$$

In natural lakes, acidic or limed, the carbon dioxide partial pressure will usually be much less than 0.3 atm, and the expression for the dissolution rate at pH values below 5.5 may be simplified to

$$R = k_1(\text{H}^+) \quad (\text{kmol/m}^2\text{s}) \quad (2)$$

and at pH values between 5.5 and 8,

$$R = k_1(\text{H}^+) + k_W - k_B(\text{Ca}^{2+})(\text{HCO}_3^-) \quad (\text{kmol/m}^2\text{s}) \quad (3)$$

where the last term takes the backward reaction at high alkalinity into account, and k_W accounts for the effect of the reaction with water and carbon dioxide. In open systems this

may be approximated as a constant factor.

Several coupled mechanisms will influence the dissolution rate of calcite from the bottom: (1) the dissolution of calcite and a subsequent increase in the pH value due to the neutralization of the acid, (2) owing to the increase in pH value, occurrence precipitation of humates and metal complexes on the calcite surfaces and inhibition of the dissolution of calcite, and (3) owing to the increase in the calcium concentration in the water column, entrance of calcium into ion exchange with hydrogen ions in the sediments.

The dissolution rate for calcite in the lake sediment may be expressed as

$$-(dm/dt) = R A B(t) \quad (\text{kmol/s}) \quad (4)$$

where R is the reaction rate and A the available mineral surface area for dissolution and $B(t)$ the deactivation function. If the area is expressed as a fraction of the lake bottom area, for the simple case where the reaction takes place far from calcite saturation, we may use a truncated form of equation (3) to obtain

$$-(dm/dt) = (k_f(H^+) + k_w) A_L P B(t) \quad (\text{kmol/s}) \quad (5)$$

The sorption of calcium to the sediments will be diffusion limited, and the exchange rate can be described by

$$-(dS/dt) = k_A A_S (Ca^{2+}) - k_S S \quad (\text{kmol/s}) \quad (6)$$

where k_A is the adsorption rate coefficient and k_S the desorption rate coefficient. The area active in sorption is A_S , the sediment surface area without calcite cover.

HYDROLOGY OF CHEMICAL LAKE REACTORS

The hydrology of most lakes varies substantially with the seasons. The two main reasons for this are the seasonal variations in the tributary flow rate and the thermal stratification of lakes.

The stratification may in shallow lakes reach such a depth that the volume under the thermocline, the hypolimnion, becomes small compared to the total lake volume. In such a case the stratification of the lake will have little influence on residence time variations in relation to the influence caused by the tributary flow rate variation. Such a system may well be modeled as a stirred tank reactor with variable flow rate.

The residence time distribution will be influenced by both the stratification and the flow variations in deeper lakes with short residence times. A two-tank reactor model will be able to describe the system in which the two tanks are merged at every turnover and the flow rate varies with the seasons.

In deeper lakes where the residence time is considerably longer than each stratification period, the lake may be considered to be fairly well mixed during one residence time period. Accordingly, the lake may be modeled with a one-tank model with variable flow rate. Stagnant zones or separated basins generally contain a very small fraction of the lake volume or the water exchange is not sufficiently restricted over the actual time periods involved.

MODEL STRUCTURE

On the basis of the considerations discussed above, two model structures of different complexity were designed in order to model the lake reacidification process after liming. The first and the simplest structure is shown in Figure 1 and models each lake in a system as a stirred tank with variable inlet flow rate.

The more complex structure is shown in Figure 2 and accounts for the stratification by modeling each lake as two stirred tanks with variable inlet flow rate. The model is reduced to a one-tank model at every turnover when the lake is completely mixed. The model will calculate the position of the thermocline, and the water is exchanged across it.

The seasonal runoff variations may be divided into different

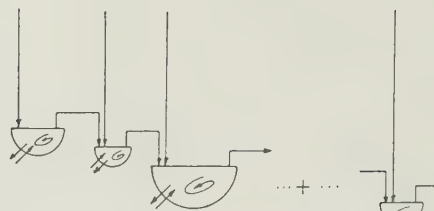


Fig. 1. A simple model may simulate a series of lakes as a series of stirred tank reactors with variable flow and chemical reaction on the tank walls.

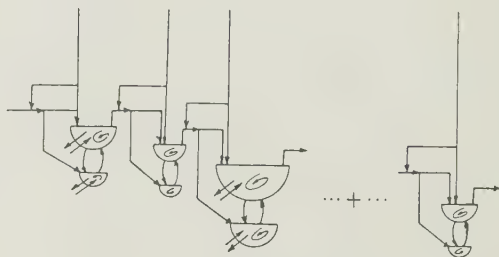


Fig. 2. A more complicated structure is needed when the stratification of lakes are to be considered. Each lake is modeled as two-tank reactors during the stratification period which are merged at every turnover.

classes. The classification of Gottschalk *et al.* [1979] was simplified into three types of seasonal runoff regimes: (1) variations typical of coastal regions, (2) variations typical of inland regions, and (3) variations typical of mountain regions. All three types are shown in Figure 3, and the geographical region to which they apply is shown on the map in Figure 4.

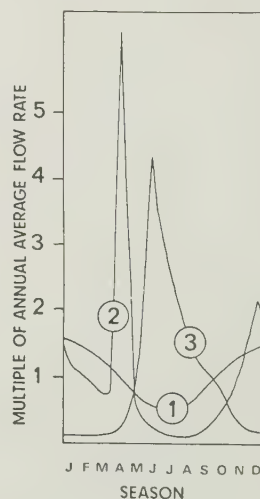


Fig. 3. The three seasonal variation types used in the model is a simplification of classifications introduced by Gottschalk *et al.* [1979]. They apply for 1, coastal regions; 2, inland regions; and 3, mountain regions. The location of these regions in Scandinavia are shown on the map in Figure 4.



Fig. 4. The map shows to which region the different runoff variation types used in the model apply. They are 1, coastal regions; 2, inland regions; and 3, mountain regions.

MASS BALANCES USED

For each tank in the model structure a complete mass balance is made for the components to be calculated. The inlet flux from the tributaries plus the amount dissolved or neutralized (dm/dt) is balanced by the accumulation in the lake volume V plus the amount sorbed to the sediment (dS/dt) plus the outlet flux:

$$(Q_i C_i) + (dm/dt) = V(dC/dt) + (dS/dt) + Q_u C \quad (\text{kmol/s}) \quad (7)$$

where the sum of the discharge of n tributaries is assumed to be equal to the outlet flow:

$$\sum_{i=1}^n (Q_i) = Q_u \quad (\text{m}^3/\text{s}) \quad (8)$$

The lake volume is assumed to be constant, which is nearly true for deeper lakes and more approximate for shallow lakes. Each tank is assumed to be well mixed, and the concentration in the lake is assumed to be equal to the concentration at the outlet.

The mass balance may be rephrased to a differential equation:

$$(dC/dt) - [(dm/dt) - (dS/dt)]/V + \left(C - \sum_{i=1}^n C_i \right) Q_u / V = 0 \quad (\text{kmol/m}^3 \text{ s}) \quad (9)$$

where the dissolution (dm/dt) is given by (5) and the sorption (dS/dt) by (6). The calcite deactivation function is usually approximated with an exponential expression [Sverdrup *et al.*, 1984a]. It was chosen to work with the mass balances for hydrogen ion and calcium, to calculate the alkalinity from a titration curve, to assume that the carbonate system is approximately at equilibrium in the water column, and to consider the alkalinity as dependent on the concentrations of the hydrogen ion and calcium. The lake was also assumed to be an open system to the atmosphere with respect to carbon dioxide.

NUMERICAL CALCULATIONS

A computer code was written to solve the differential equations numerically with the Runge-Kutta algorithm and calculate the reacidification of a limed lake. The code was written for a small personal computer to facilitate model availability.

The simple model structure will need the following input data which are among those usually provided in Swedish lake liming projects or may be easily estimated from the following: (1) initial pH in the lake after liming, (2) annual average pH in the tributary, (3) initial calcium concentration after liming (in milligrams per liter), (4) average calcium conc in the tributary (in milligrams per liter), (5) amount of calcite on the bottom of the lake (tons), (6) fraction of the bottom covered by calcite (in percent), (7) mean lake depth (in meters), (8) lake volume (in 10^6 m^3), and (9) average residence time (in years). For all Swedish lake liming projects, plans are made that describe the total amounts of calcite to be spread and its spatial distributions over the lake surface. The amount on the bottom may be estimated from the total amount distributed and the amount instantly dissolved. The fraction of the bottom fully covered by calcite may be estimated from the spatial distribution of calcite powder over the lake surface and the amount on the lake bottom [Sverdrup *et al.*, 1984a].

In addition, the tributary flow variation type is indicated with a number that can be read from the map in Figure 4: (10) tributary flow variation type. If whole series of lakes are to be modeled the modeler needs to know the fraction of the tributary input coming from an upstream modeled lake (as in data). The deactivation rate for calcite on the bottom and the sorption rate were kept constant internally in the model. The deactivation rate has been determined from large amounts of lake liming data [Sverdrup and Bjerle, 1983; Sverdrup *et al.*, 1984a, b; Bengtsson *et al.*, 1981] and was set at 0.6 y^{-1} .

CALCULATIONS FOR THE LAKES JELLUNDEN AND NEDRE SÄRNAMANNASJÖN

The model was used to calculate the reacidification of lake Jellunden in the province of Halland in southwest Sweden [Sverdrup *et al.*, 1984a]. The lake was limed in 1980 with 1800 tons of calcite powder classified as 0–0.2 mm; 1400 tons were spread in the lake, mostly in the littoral zone; the rest was spread as coarse gravel in a tributary. Experiences from the Swedish Experimental Liming Program [Bengtsson *et al.*, 1981] indicate that liming with coarse gravel seldom works, and accordingly it was assumed that the gravel had no significant effect on the lake chemistry.

The bathymetric map of Jellunden, based on 97 measurements (Figure 5), was used to make the hypsographic curve in Figure 6 for the lake. It indicates that the volume of an eventual hypolimnion will be small compared to the total lake volume if it is assumed that the thermocline reaches a depth of 6–8 m. This allowed us to use a one-tank model for the calculation.

The data needed for the calculation are listed in Table 1. The lake was monitored by the local authorities from the date of liming till the reliming in late 1983. These data for pH, alkalinity, and calcium are shown together with the calculated values in Figure 7.

Lake Nedre Sernamannasjön is a mountain lake in the province of Dalarna, Sweden. It is rather small and has a short residence time, 0.3 years. The lake was limed in October 1977 with 44 tons of a coarse calcite powder classified as 0–1 mm. Half the amount was spread in the lake, and the rest was spread on land around the lake. The lake chemistry was monitored by the Swedish Environmental Protection Agency after the liming of the lake.

The input data used for the calculation of the reacidification are found in Table 1. The observed pH and calcium con-

TABLE 1. Input Data Used in Model Calculation of the Reacidification of the Lakes Jellunden and Nedre Sernamannasjön

Data	Jellunden	Nedre Sernamannasjön
Initial pH after liming	6.5	6.7
Average pH in the tributary	5.0	5.1
Calcium concentration after liming	6.0 mg/L	3.6 mg/L
Calcium concentration in the tributary	2.8 mg/L	0.4 mg/L
Lake volume	$37.5 \times 10^6 \text{ m}^3$	$0.66 \times 10^6 \text{ m}^3$
Lake depth	4.4 m	2.0 m
Residence time	1.45 years	0.3 years
Amount calcite on the bottom	1000 tons	20 tons
Fraction of the bottom covered by calcite	7%	5%

The data are actual physical and chemical data estimated from the records kept at the Swedish National Board of Fisheries and the Swedish Environmental Protection Agency.



Fig. 5. Bathymetric map of the lake Jellunden in the province of Halland. The map is based on 97 shots in the lake.

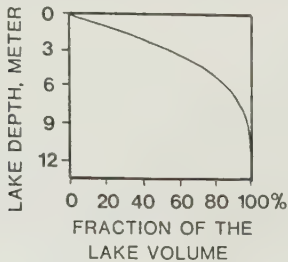


Fig. 6. Hypsographic curve for the lake Jellunden based on the bathymetric map. It may be seen that the volume beneath the 6 m line is very small, making the hypolimnion of the lake less than 10 percent of the total volume.

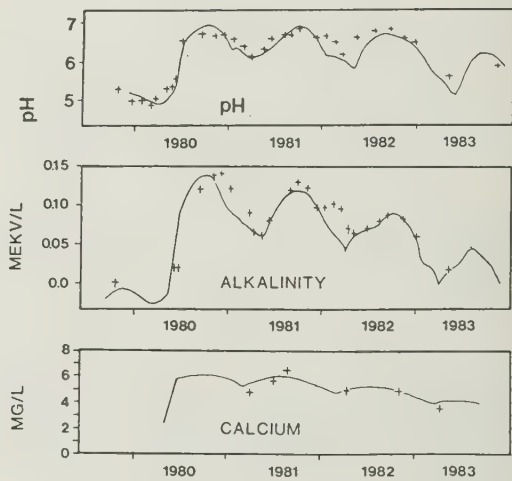


Fig. 7. The model calculation for the reacidification of Jellunden is shown by the bold line, together with the observed data (crosses).

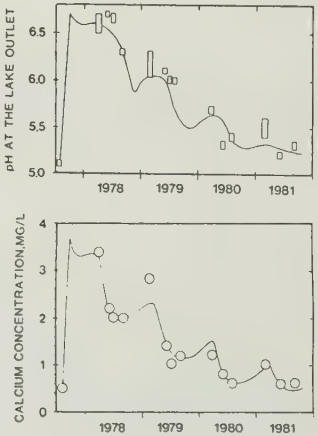


Fig. 8. The calculated pH and calcium concentrations for Nedre Sernamannasjön (solid curve) shown together with the observed values (open circles). The residence time for the lake is approximately 0.3 years. The bars indicate inaccuracies in the measurements.

centrations are shown together with the calculations in Figure 8. It can be clearly seen that the calculations follow the observations accurately.

STRATIFICATION MODEL

The more complicated model structure shown in Figure 2 may be used to calculate the reacidification of a stratified lake. This model structure requires some additional data in order to work: (1) pH in the epilimnion after liming, (2) pH in the hypolimnion after liming, (3) calcium concentration in the epilimnion after liming (in milligrams per liter), (4) calcium concentration in the hypolimnion after liming (in milligrams per liter), (5) average pH in the tributary, (6) average calcium concentration in the tributary (in milligrams per liter), (7) amount of calcite on the lake bottom (in tons), (8) fraction of the epilimnic bottom covered by calcite (in percent), (9) fraction of the hypolimnic bottom covered by calcite (in percent), (10) mean lake depth (in meters), (11) maximum lake depth (in meters), (12) lake volume (in 10^6m^3), (13) residence time (in years), (14) lake surface area as a fraction of the watershed area, and (15) tributary flow variation type. This model does not have the same practical applicability in operational liming as the simpler model, as the complete set of input data needed is available only in a few special liming projects. The model was used to calculate the initial stages after the liming of the lake Lysevatten near the city of Göteborg on the Swedish west coast. It is a clear water lake of medium size, an average depth of 4.7 and a maximum depth of 17.

Lysevatten was limed in May 1984 with 60 tons of "T-slag", an industrial waste product composed of different calcium silicates. The dissolution kinetics of "T-slag" appear to be similar to the kinetics of calcite [Sverdrup, 1983a]. The lake was limed mainly in the littoral zone, which caused neutralization of the epilimnion only. The hypolimnion remained acidic from the liming in May 1974 until the turnover in the fall the same year. The chemistry of the lake was carefully monitored by Hultberg [1982] of IVL in Göteborg from 1973 until present.

A calculation for the lake was done, using the data in Table 2. The stratification becomes less important for the later stages of the reacidification as the residence time of the lake, 3.7 years, spans over several turnover times. The calculation for the calcium concentration after liming is shown in Figure 9 together with the observations. The transport across the thermocline was modelled as turbulent diffusion across a boundary layer [Warfvinge et al., 1983]. It can be seen that the concentrations in the epilimnion and the hypolimnion will converge after approximately one residence time.

TABLE 2. Input Data Used for Model Calculation for Lake Lysevatten

	Value
pH in the epilimnion after liming	7.4
pH in the hypolimnion after liming	5.0
pH in the tributary	4.9
pH of the precipitation	4.2
Calcium concentration in the epilimnion after liming	7.4 mg/L
Calcium concentration in the hypolimnion after liming	1.7 mg/L
Calcium concentration in the tributaries	1.6 mg/L
Calcium deactivation rate	0.8 yr^{-1}
Mean lake depth	4.7 m
Maximum lake depth	17.0 m
Lake volume	$1.9 \times 10^6\text{ m}^3$
Lake surface as fraction of the watershed	33.0%
Amount calcite on the bottom	30 tons
Fraction of the epilimnic bottom covered by calcite	25%
Fraction of the hypolimnic bottom covered by calcite	0%

The data are actual estimates from Hultberg and Andersson [1982].

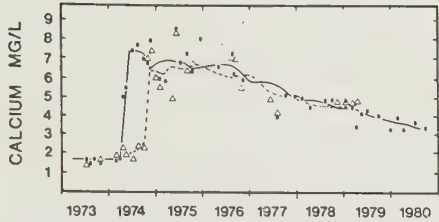


Fig. 9. The initial stages after liming in the lake Lysevatten on the Swedish west coast. The lake was limed in the littoral zones only, neutralizing the epilimnion but not the hypolimnion. The figure shows the calculated calcium concentration (solid curve) and the observed data for the epilimnion (solid squares) and in the hypolimnion (dashed curve and triangles).

The sediments not receiving calcite consumed calcium and alkalinity from the water column, as only a small fraction of the lake bottom was covered with calcite. In Lysevatten it may be calculated that the sediments consumed approximately 0.2 tons calcite per hectare, which is in good agreement with what can be observed in other lakes [Sverdrup and Warfvinge, 1984b].

DISCUSSION

The simple model structure gives rather accurate predictions for the reacidification of limed lakes. It may be used to relate the residence time of a lake to the time required to reacidify a limed lake to pH 6.0, which the Swedish authorities define as the point for reliming [Bengtsson et al., 1981]. Figure 10 indicates the observed reacidification time for limed lakes. The curve is valid for bottom dosages in the range 0.2–1.3 ton calcite per hectare.

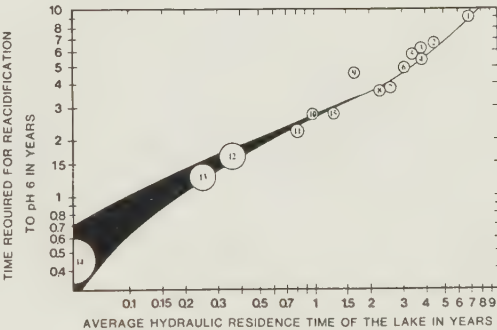


Fig. 10. The time required for an average limed lake to reacidify to pH 6.0 may be read as dependent on the residence time for the lake. The diagram was calculated for a lake with a volume of $1.5 \times 10^6\text{ m}^3$ and 5 m average depth with the model. The numbered circles represent observed reacidification times for the lakes: 1, Hornäsön; 2, Övre Bolsjön; 3, Lysevatten; 4, Smedvatten; 5, Skitjern; 6, Blomman; 7, Södra Blötevatten; 8, Bredvatten; 9, Stensjön; 10, Grytsjön; 11, Ekelidvattnet; 12, Nedre Sernamannasjön; 13, Tarmälängen; 14, Kolabodasjön; 15, Jellunden. The lake volume in the lakes vary from 0.4 to $37.5 \times 10^6\text{ m}^3$ and the depth from 2 to 15 m. Lake liming will hardly produce a stable result in lakes with residence times shorter than half a year. In such lakes strategies for liming running waters may be more successful. Lakes with residence times longer than 3 years will have their reacidification rate mostly determined by the flushing rate. The diagram applies to a bottom cover of calcite, P from 0.05 to 0.30 and a bottom residual of calcite between 0.2 and 0.8 ton/ha.

By doing a sensitivity analysis for the different parameters, those with the strongest influence on the reacidification rate may be identified. The four most important factors determining the reacidification rate may be identified as hydrological residence time, amount of calcite on the bottom, fraction of the bottom with calcite cover, and acidity of the tributaries. Other important parameters are stratification, sediment ion exchange, calcite deactivation rate, and supply of acidic organic matter with the tributaries. These are of lesser importance compared with the first four or do not vary very much between the different limed lakes.

Figure 11 is a drawing of the response surface for the reacidification in terms of hydrological residence time and the fraction of the bottom with calcite cover. It can be seen that there is a maximum in reacidification time. Optimally, the fraction of the bottom with calcite should be 0.25–0.50. It can be seen that to limit the calcite distribution to the littoral zone only, which leads to a calcite bottom cover in the range 0.05–0.10, is far from optimal.

An indication of the importance of the amount of calcite on the bottom is given by Figure 12. It shows the response surface for the reacidification time in terms of hydrological residence time and amount of calcite on the bottom.

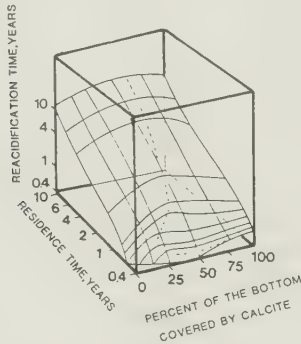


Fig. 11. The response surface for the reacidification time in terms of hydrological residence time and fraction of the bottom with calcite cover after liming (P).

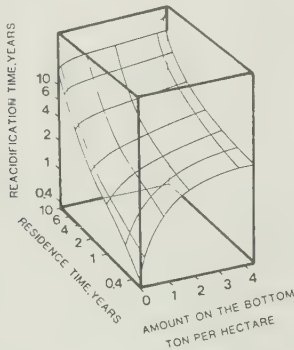


Fig. 12. The response surface for the reacidification time in terms of hydrological residence time and amount calcite on the bottom after liming.

Studies of limed lakes with the model and a survey of data from lake limings allow us to divide the diagram in Figure 11 into three zones. In lakes with residence times longer than 3 years, the residence time will be substantially longer than the deactivation time for calcite on the bottom. Accordingly, the time required for reacidification will be mainly determined by the flushing rate and calcite dissolving from the bottom will be of less importance.

Residence times between 3 years and 1/2 year will be of approximately the same order of magnitude as the calcite deactivation time. For such lakes the dissolution will be able to prevent reacidification the first year after liming, after which the flushing rate will be the main determining factor for the reacidification rate.

For lakes with residence times shorter than 1/2 year, lake liming does not necessarily produce a stable result. The pH shocks may break through in the system at periods with high flow and ruin the liming result. Such lakes are often more adequately treated with methods for the liming of running water.

Studies of integrated mass balances for limed lakes [Sverdrup and Warfvinge, 1984b] together with model studies indicate the 1–2.0 tons of calcite per hectare lake bottom will be able to dissolve before the deactivation virtually brings the dissolution to a halt. This stresses the fact that it is of no use to pile large amounts of calcite on the lake bottom or in narrow littoral zones and hope it will dissolve. The limited amount of wave actions in the littoral zone of a lake is far from enough to prevent the deactivation to take place [Sverdrup et al., 1984a].

It is important that the model works with physical parameters that can be easily determined. No calibrations or “rubber parameters” are needed. This strengthens the general applicability of the model.

Having identified the most important parameters for the reacidification rate, the model may be used to make a general diagram for predicting the approximate time required for reacidification of a lake. In Figure 13 an attempt has been made to combine some of the most important parameters. The time for reacidification may be read from the diagram as a function of the hydrological residence time and the calcite load factor B , defined as

$$B = (M_B/A_L \times P/0.20) \text{ ton/ha}$$

where M_B is the amount of calcite on the bottom, to the lake surface area, and P is the fraction of the bottom area with calcite cover.

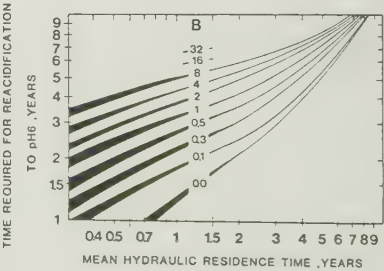


Fig. 13. General diagram to estimate the reacidification time. The factor B combines the effect of the residual amount calcite on the bottom after liming, the fraction of the bottom area with calcite cover and sediment–lake water interactions. B is defined as $(M_B/A_L)(P/0.20)$ and expressed as ton calcite per hectare.

NOTATION

$\sum_{i=1}^n a_i$	sum of all elements from a_1 to a_n ; $a_1 + a_2 + \dots + a_n$.
A	calcite surface area, m.
A_L	lake bottom area, m ² .
A_S	lake bottom participating in sorption, m ² .
$B(t)$	deactivation function.
C	concentration, kmol/m ³ .
C_i	concentration in tributary i , kmol/m ³ .
i	index.
K_1	mass transfer coefficient for hydrogen ion, m/s.
K_2, K_3	mass transfer related reaction rate coefficients.
K_A	adsorption coefficient, m/s.
K_D	desorption coefficient, m/s.
K_B	dissolution back reaction coefficient, m ⁴ /kmol s.
K_W	reaction rate coefficient for water attack, kmol/m ² s.
m	mass.
M_B	amount calcite on the bottom after liming, ton.
n	number of tributaries.
P	calcite surface area as fraction of the lake bottom surface area.
Q_i	flow rate in the tributary i , m ³ /s.
Q_u	flow rate at the lake outlet, m ³ /s.
R	reaction rate, kmol/m ² s.
S	sorbed amount, kmol.
t	time, s.
V	lake volume, m ³ .

Differentials

dC/dt	concentration change with time, kmol/m ³ s.
dm/dt	dissolved mass with time, kmol/s.
dS/dt	sorbed mass with time, kmol/s.

Acknowledgments. Bo Bengtsson at the Swedish National Board of Fisheries at Göteborg has helped our research very much by supplying us with large amounts of valuable information from the liming archives in Göteborg. Hans Hultberg of the IVL in Göteborg kindly helped us with data from lake Lysevatten. William Dickson at the Swedish Environmental Board supplied data from Nedre Sernamansjön. The model is written in Basic and compiled under the CP/M system, which allows it to be run on a large number of different personal computers. The model may be purchased from the authors by writing to Sverdrup and Warfvinge, Swedish International Science and Technology, Malin Gyllenkroksväg 4 S-225 90 LUND, Sweden, or in the United States to D. Britt, International Science and Technology, 1810 Mich. Farady Drive, Reston, VA 22090.

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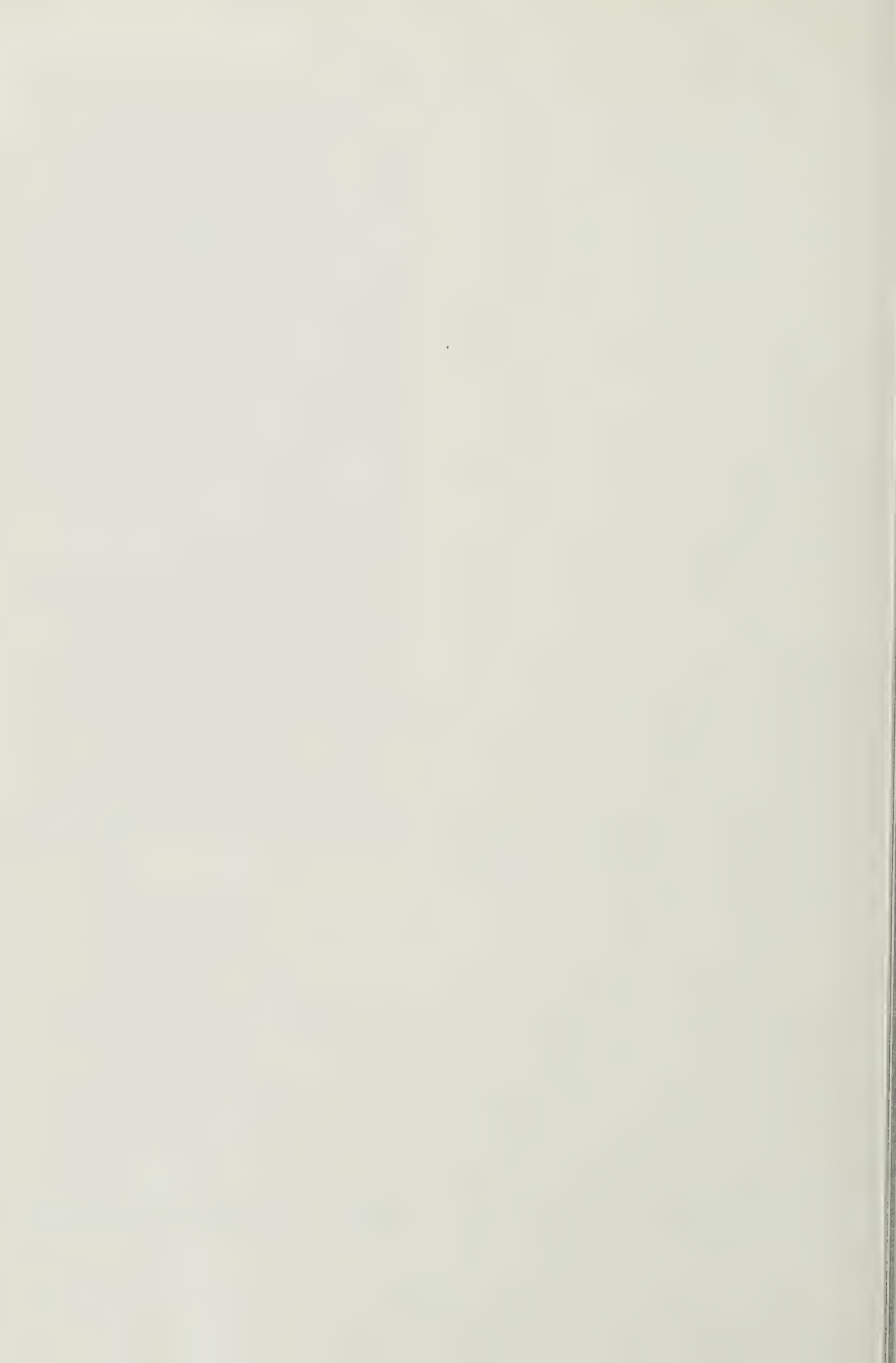
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Water Resources Research



Acidic Precipitation

CALCITE DISSOLUTION AND ACIDIFICATION MITIGATION STRATEGIES

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ABSTRACT

The dissolution kinetics of a calcite powder sinking in acidified water, and the dissolution kinetics for the long-term dissolution of calcite from the bottom, taking the deactivation into account are studied. The solutions of the differential equations are given as diagrams that can be used to predict the outcome of a treatment, and the calcite utilization. These solutions are shown to be in agreement with observation from lake liming projects. As a consequence of the verified theory, a mitigation strategy can be outlined in terms of meeting neutralization requirements and project economy. This depends on such variables as initial pH, particle size, location of treatment, water depth, and such. The acidification mitigation strategy is defined for (1) lakes and near stagnant waters, and (2) running waters. For lakes and near stagnant waters a strategy is outlined, and criteria for the neutralizing agent given. The Kalkad Calcite Distributor developed as a result is presented. For running waters a strategy is defined, and criteria given for the neutralizing agent and the location of the effort, to optimize the result and its cost. A short presentation of equipment for treating running water is given—The Fluidized Diversion Well, The Slurry Dosing Equipments and The Dry Powder Dosing Apparatus—along with data on their performance.

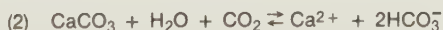
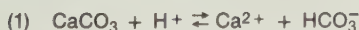
INTRODUCTION

Experience from the Swedish lake and soil liming program has clearly shown that knowledge of the mechanisms of calcite dissolution is essential in planning an acidification mitigation strategy.

Neutralizing agents other than calcite have been tried, but calcite seems to be the most economical and easiest available agent. Therefore this study will only consider calcite and the knowledge necessary to achieve desired neutralization.

CALCITE DISSOLUTION AND LIMING

The dissolution of solid calcite in dilute acid can be described as a heterogenous solid-liquid reaction. The chemical reactions involved are:



In natural waters with a pH-value less than pH 6.5, reaction (1) will dominate, and for values above pH 6.5 reaction (3) will be important. In most cases the natural waters considered for liming will contain too little dissolved carbon dioxide for reaction (2) to be of any importance.

The dissolution rate for calcite under different conditions has been shown to be controlled by diffusion of the reacting species (Sverdrup, 1982, 1983a; Sverdrup and Bjerle, 1983).

It is also necessary to distinguish between two cases which lead to different kinetic expressions: During the initial stage of a liming operation, the calcite

powder sinks through the water column. The dissolution rate will be rapid compared to calcite resting on the bottom. There, the diffusion boundary layer will be several orders of magnitude larger and the dissolution rate accordingly slower. In addition, the stagnant conditions will permit precipitates to form on the calcite surfaces and thus further reduce the dissolution rate.

INITIAL DISSOLUTION IN LAKE LIMINGS

When a calcite powder is spread in a lake, the particles will rapidly sort out according to size and sink through the water column and dissolve. This process is in detail described earlier (Sverdrup, 1983a). The process is controlled by diffusion of the hydrogen ion and

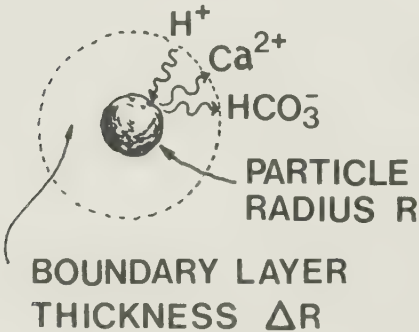


Figure 1.—Dissolution model for a single spheric particle.

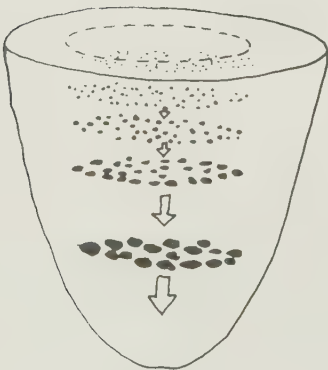


Figure 2.—Dissolution model for a calcite powder sinking in a lake. The largest particles will sink the fastest and partly dissolve and elevate the pH-value before the next particle size.

the governing differential equation may, for the dissolution of one particle as in Figure 1, be written:

$$-\left(\frac{\partial M}{\partial t}\right) = D \cdot \left(\frac{\partial C}{\partial R}\right)_R \cdot A_P \cdot M_E \quad (1)$$

which means that the mass dissolved is proportional to the surface of the particle, and the flux of hydrogen ions into this surface. When it is considered that a powder consisting of many different particle sizes is sinking in acidic water as illustrated in Figure 2, the equation becomes:

$$-\frac{d}{ds} \sum_{i=1}^n M_i = A \cdot \sum_{i=1}^n \frac{\Delta \phi_i}{R_i^3} \left(\Delta H^+ - \sum_{j=i-1}^{n-1} \left(\frac{M_o - M_j}{AL \cdot P \cdot S \cdot M_E} \right) \right) \quad (2)$$

This equation can be solved analytically and expressed as the dissolved fraction X:

$$X = A' \cdot \Delta H + S \cdot \sum_{i=1}^n \frac{\Delta \phi_i}{R_i^3} \left(1 - \left(1 + \left(\sum_{j=i-1}^{n-1} j \right) \cdot B + \left(1 + \sum_{j=i-1}^{n-2} \left(\sum_{j=i-1}^{n-1} j \right) \cdot B^2 - \dots + (-1)^{n-i} \cdot 1 + \sum_{j=i-1}^1 \sum_{j=i-1}^{n-1} \sum_{j=i-1}^{n-1} j \dots B^n \right) \right) \right) \quad (3)$$

where B is the calcite surface load factor $B = A' \cdot M^* / P \cdot M_E$. This general solution can be simplified for lake limings into diagrams such as in Figure 3. The diagram is valid for a water depth $S = 5$ meter but, as can be seen from the solution, other depths can be accounted for by compensations in the entering pH-value in the diagram.

The solution of the differential equation is also available as a program for a desk computer. The in-data required are: initial pH, sinking depth, calcite dosage per m^3 , fraction of the lake surface treated, and the particle size distribution if this does not match one of the built-in standards. The titration curve is also required as grams calcite needed to raise pH one unit in one m^3 .

Figure 4 shows how well the theory agrees with the experience from Swedish lake limings (Sverdrup and Bjerle, 1983).

In running water, the turbulence of the water will tend to increase the sedimentation time and thus enhance the "instant" dissolution of calcite. The effect will be more important for the smaller particles and less pronounced for the coarser. Hence, the intermediate calcite powders will be influenced most as the finer powders dissolve almost completely while the coarser powders contain much material too coarse to be greatly influenced.

From the theory it can, as in several liming projects, be deduced that the most important factors governing the initial dissolution are:

- The initial pH-value in the water column,
- The sinking depth for the powder,
- The particle size distribution or the fineness of the calcite powder used, and
- The intensity of the dosage, as amount calcite per m^2 limed.

A close study of the solution equation shows that a high initial pH-value in the water column can, in order to maintain a good calcite utilization, be compensated for by choosing an application site with greater depth. Waters with high initial pH-value or lesser depth, as for instance running waters, can be compensated for by choosing a more finely ground powder.

A high dosage intensity will tend to lower the dissolved fraction by local saturation or complete neutralization. This may be countered by spreading the powder over a larger part of the water surface (Sverdrup et al. 1983).

It is also of importance that the powder is well mixed and suspended in water when spread. In a normal dry calcite powder the smaller particles will adhere to the surfaces of the larger ones. If not well suspended in water prior to liming, the larger particles will carry the smaller and, accordingly, the powder is not efficiently utilized. This can be seen in Figures 6 and 7, which show a dry calcite particle and one of the same size picked from a suspension in water. It can clearly be seen how the surface of the dry particle is covered with smaller ones.

LONG TERM DISSOLUTION OF CALCITE

Calcite resting on the bottom is under hydrologically stagnant conditions compared with their sinking phase. The diffusional boundary layer is several orders of magnitude larger and the dissolution rate accordingly slower even in river beds and littoral zones of lakes.

Such stagnant conditions will also allow precipitates of aluminum and iron and biological growth on the calcite surface to form, and thus impede the dissolution further. If the calcite is viewed as a sheet resting on the bottom, the part that dissolves downward will be bound into the sediment and released only when all overlying calcite is dissolved. This implies that only a fraction of what is resting on the bottom is available to the water column and also only for a limited period of time. This can be very clearly seen in Figure 8 which shows an integrated mass balance for the lake Övre Bolsjön which was limed in 1976 with 500 tons of calcite ground to 0-0.5 mm (no. 6). The first stage, A, represents the initial dissolution during sinking, that is 38 percent of the total amount. The long term dissolution, B, constitutes approximately 5 percent of the total amount or 8.5 percent of the amount left on the bottom.

It can here be seen, as in many other cases, that the calcite deposited on the bottom is poorly utilized and does not give a pronounced long-term effect in this case. Approximately 50 percent is "lost" on the bottom.

The kinetics for the long-term dissolution can be described with an expression of the following type:

$$-\left(\frac{\partial m}{\partial t}\right) = \left(\frac{\partial F}{\partial t}\right) + \left(\frac{\partial S_x}{\partial t}\right) \quad (4)$$

$$\left(\frac{\partial F}{\partial t}\right) + \left(\frac{\partial S_x}{\partial t}\right) = D \cdot \left(\frac{\partial C}{\partial X}\right)_x \cdot A L \cdot \psi(t) \cdot P \quad (5)$$

where $\psi(t)$ is a deactivation term taking care of the inhibition of the calcite surfaces and the sedimentation of detritus, and $(\partial S_x / \partial t)$ a term for the adsorption-desorption rate of calcium to the sediments. $(\partial F / \partial t)$ is the net flux of calcium from the bottom covered with

calcite. Based on the dissolution kinetics and on the mass balance, a reacidification model was made for limed lakes. A test run for the lake Övre Bolsjön is shown in Figure 9 with predictions and observations on the pH, the alkalinity, and the calcium.

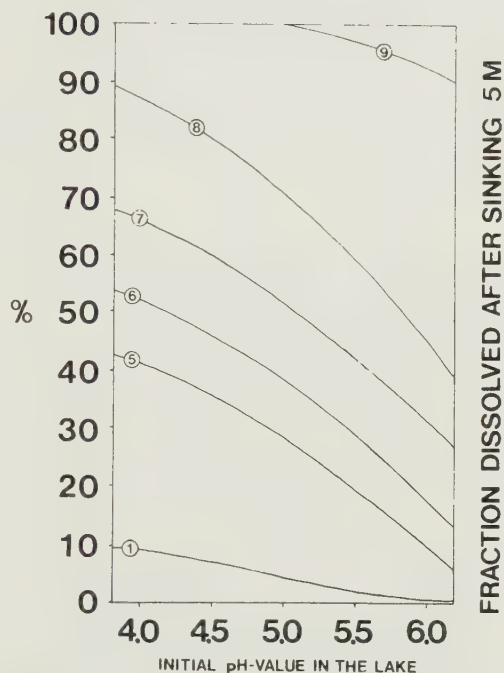


Figure 3.—The dissolved fraction X for different calcite powders as shown in Figure 5 versus initial lake pH. The diagram is valid for a sinking depth of 5 meters, but this may be compensated for other depths with the equation: $pH_{\text{diagram}} = pH_{\text{initial}} - \log_{10}(S/5.0 \text{ m})$.

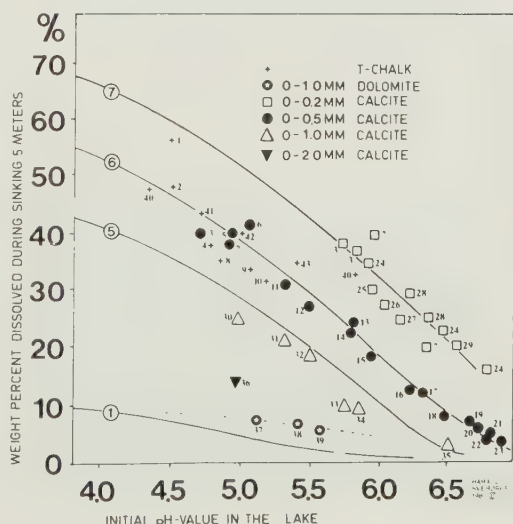


Figure 4.—The dissolved fraction X observed in several Swedish lake liming projects as compared to the theoretical calculations.

Figure 8 shows the dissolution of calcite together with the integrated mass balance. In this case, as well as in several others tested at the Institute of Technology in Lund, the model seems to predict the reacidification of the lake very well. The model is available at the Institute of Technology in Lund and runs on a small desk computer that makes calculations for whole lake systems.

In Sweden it has been considered that the water movements over hard lake bottoms or in the littoral zone could enhance the dissolution. In terms of diffusion resistance, however, this has negligible effects. In these areas lack of sediment makes the downward

diffusion into the sediments as well as the adsorption/desorption of calcium very small; hence, a larger fraction of calcite is available to the lake water.

SPECIFICATION OF CALCITE POWDERS FOR LIMING

Technically all powders can be well defined by the particle size distribution, and accordingly, the specifications should be tied to the particle size distribution curves. Commercial names may be misleading. It is of economic importance that the calcite is well utilized in relation to its application price. An economic analysis of the experiences from Swedish liming operations show that calcite powders coarser than no. 5 in Figure 5 will give low cost efficiency. In general, the calcite powders marked nos. 6, 7, 8, or 9 will be the most cost efficient in lake limings, and nos. 7, 8, 9, or 10 best for running water. The exact optimum can be calculated as the lowest neutralization cost which is the application cost divided by the fraction calcite utilized.

LIMING ON LAND

Liming on land has been tried as a method to treat surface waters. These efforts have not always been successful and the dissolution efficiency of calcite in relation to the target water was rather low.

The dissolution rate differential for calcite in soil is of a type similar to equation 4, but the dynamics of the system are quite different as soil limings are most often performed in the unsaturated zone with a periodical infiltration flow of an intermittent nature. In lake bottoms the conditions for mass transfer are those of a stagnant saturated system.

The dynamics of the dissolution and the leaching of the soil do not follow the dynamics of the watercourse flow, hence massive efforts are needed to produce any effect.

Acid soils are greatly depleted of calcium ions, and before any substantial amount can be leached to the runoff, the calcium will be adsorbed by the soil to fill this deficiency—in fact neutralizing the soil. This explains why several land limings, intended to affect surface water, do not work.

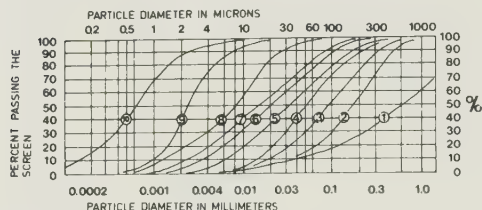


Figure 5.—Particle size distribution curves for several calcite powders used in Swedish liming projects. Some of their commercial names are: 1: Agricultural limestone, 6: 0–0.5 mm calcite powder, 7: 0–0.2 mm calcite powder, 9: Malmö Chalk powder.

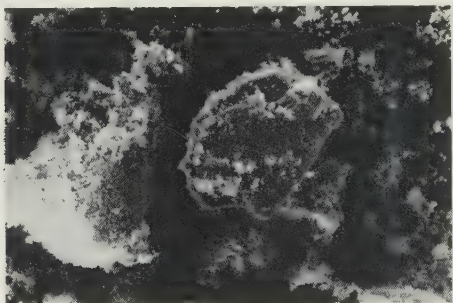


Figure 6.—A sample of dry screened calcite powder. It can be seen that the smaller particles adhere to the surface of the larger ones. If the powder is not well suspended in water prior to liming, the smaller particles will follow the larger ones as they sink.

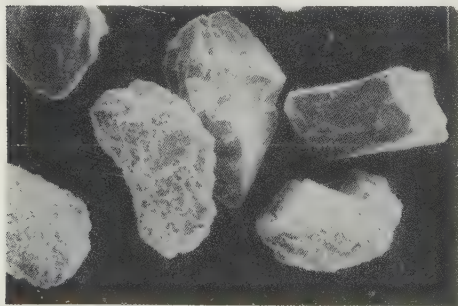


Figure 7.—A sample of calcite particles from a powder suspension enlarged 200 times. It can be seen that no more small particles adhere to the larger.

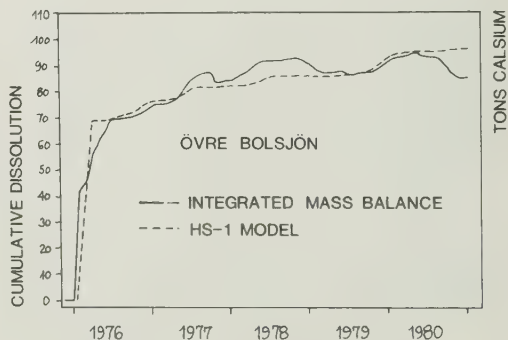


Figure 8.—An integrated mass balance for Lake Övre Bolsjön on calcium. The lake was limed in 1976 with 500 tons of powder no. 6 of calcite. Simulation of the integrated mass balance for calcium is marked with the dotted line.

American studies (Meyer and Volk, 1952) show that particles larger than 0.3 mm in diameter are of very little value in soil limings. Accordingly, the coarse powders, often used in soil limings, demand heavy doses.

A MITIGATION STRATEGY OUTLINED

It is of importance when a liming project is planned that the decisions taken are adequate and proceed in the right order, as they depend upon each other. The flow sheet in Figure 10 tries to identify the most important steps and their best order.

The target water for the liming project should first be characterized in terms of neutralization need as dissolved calcite. This may either be done by titration or calculated theoretically, taking precipitation of aluminium and iron complexes and such factors into account. Wright (1983) gives an example of the procedure.

The next step will be to calculate the total dissolved calcite needed in the project. It will depend on the volume of the lakes to be limed, the flow rate of the river to be limed, or the amount of soil to be limed and neutralized.

The actual amount to be used for the neutralization is the amount calculated from the physical and chemical conditions of the location. For a lake this can be expressed as:

$$M = \frac{V_L \cdot \left(\frac{dM}{dpH} \right) \cdot \Delta pH}{X \cdot Y} \quad (6)$$

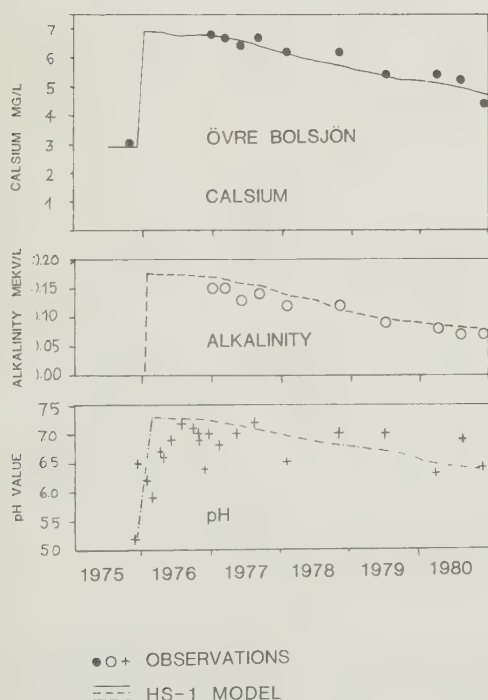


Figure 9.—Predictions made with the reacidification model as compared to the observations.

The lake volume V_L times the neutralization need (dM/dpH) expressed as gram calcium carbonate per pH-unit and m^3 , times the needed pH-value elevation will give the theoretical amount needed as dissolved calcium carbonate. When this is divided by the dissolution efficiency X and the content of calcium carbonate, Y , in the calcite used, the actual amount to be added is calculated. For a river the calculation becomes:

$$M = \frac{1}{Y} \left(\frac{Q_i \cdot \left(\frac{dM}{dpH} \right) \cdot \Delta pH_i}{X_i} \right) \quad (7)$$

where Q_i is the volume of runoff for a period of time in which the pH-value elevation needed is ΔpH_i , and the dissolution efficiency, X_i , under the circumstances. As the conditions in a river may vary considerably, the calculation will have to be made for shorter periods and added together as in equation 7.

Several possibilities for methods and localization of the neutralization may be suggested. For these alternatives, the result must be estimated in terms of chemical result and duration of a satisfactory condition in the system. For lakes, a diagram as in Figure 11 may be used to estimate the time needed for the lake to be reacidified to pH 6.

The expected result in terms of chemistry, biology, result stability, and duration are then compared to the intentions of the liming project. All methods and possible localizations of the neutralizing operation which cannot fulfill the intentions of the project must be refused or redesigned.

The choice will often be between methods for running water and methods for lake liming. Lakes or lake systems with very short retention times may often be successfully treated as running water. In Figure 12 a decision tree is suggested to assist in choosing a method. Usually several alternatives to carry out the neutralization and to reach a satisfactory result exist.

At this stage the total project cost or the neutralization cost efficiency is calculated for the different alternatives and the most cost-efficient alternative can thus be used.

LIMING OF RUNNING WATER: SOME EXAMPLES

In Sweden today, there are many technique options and methods for liming running water.

The diversion well. The fluidized diversion well has been tried in laboratory experiments and since 1980 at a pilot plant at Piggaboda in Smaland, Sweden.

The working principle of the well is that of a ball-mill. Water flowing through the calcite gravel will keep the particles in rapid motion, and the mechanical wear on the particles will grind them to powder. The powder then dissolves rapidly. The mechanical wear also keeps the calcite surfaces free from precipitates which, if the particles were at rest would reduce the dissolution drastically. The apparatus takes all its energy from the water. The diversion well is shown in Figure 13. The widening at the top will lower the fluid velocity below the fluidization velocity and the particles will hence be returned to the well. In this way an

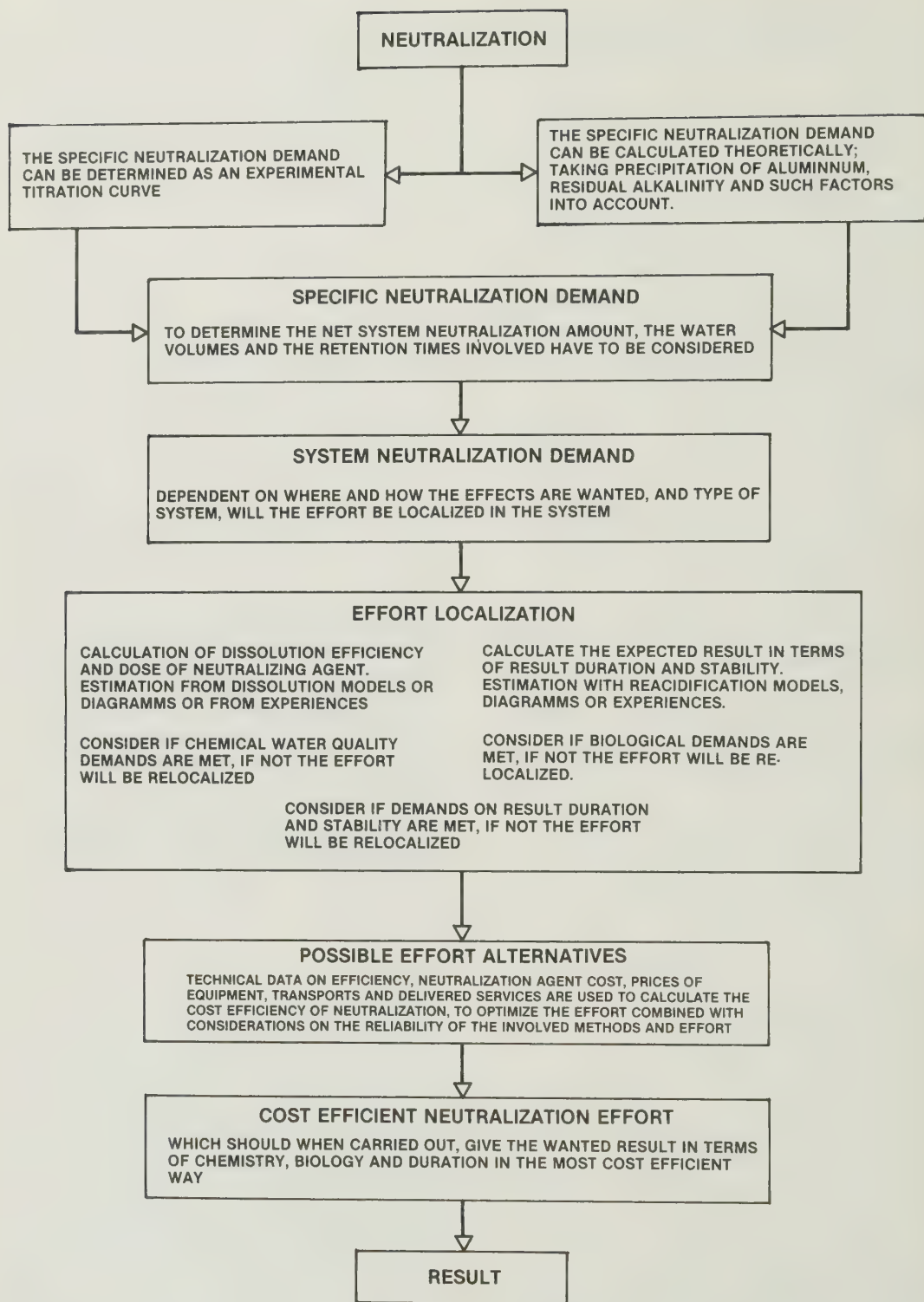


Figure 10.—Flow sheet for the planning of liming efforts.

80-90 percent utilization of the calcite mass can be achieved.

The dosage given by the well is more or less constant per m³. Experiences from Piggaboda show that approximately 5 percent of the mass in the diversion well dissolved per day, raising the pH-value by one unit.

The diversion well will function well, without freezing, down to at least -15° Celsius (see Fig. 14).

More information on the fluidized diversion well can be found in Sverdrup et al. 1983 or Sverdrup et al. 1981.

The dry-powder doser. The dry-powder doser has been successfully tried in full scale in the salmon river Fyllean, Halland, Sweden. A plan of the plant is shown in Figure 15. Calcite powder, usually of type nos. 6, 7 or 8, is stored in a large container. The automatic regulating unit will register the level of the river and relate it to the flow rate. The dry powder is mixed with water and then pumped to the river. This will ensure good suspension of the dry powder and accordingly a fair calcite utilization.

The pH-value in the river ranges from pH 4.9 to 5.9 upstream from the plant. The dosing takes place where the river is approximately 80 cm deep. During a test period, from January to May 1983, approximately 45 percent of the calcite was utilized (Fig. 16).

The slurry doser. The slurry doser has been located in the Fyllean river further downstream from the dry powder doser at Marback. The plant also contains a large tank for the wet suspension of very finely ground calcite, and a regulation unit which calculates the river flow rate from the water level. The calculations are here performed by a microprocessor containing the nonlinear pH flow rate relationship and a titration curve (Fig. 17).

The calcite suspension used contains 70 percent calcite suspended in water. The powder is extremely finely ground to a mean diameter of 0.5-2.0 microns. Such a fine calcite powder will dissolve completely even as pH-values near 7. At such pH-values the

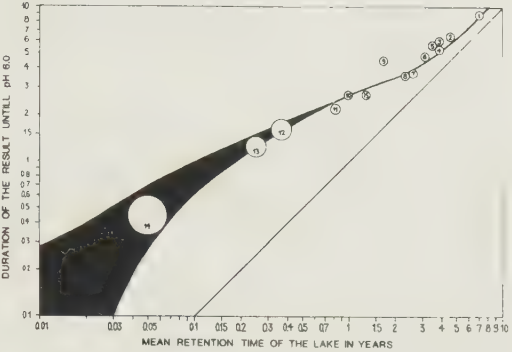


Figure 11.—The liming result duration until pH 6 plotted versus the lake mean retention time. The drawn line is the theoretical calculation made with the "HS-1" model and the circled observations from: 1. Hornasjon, Goteborg; 2. Ovre Bolsjon, Bohuslan; 3. Lysevatten, Goteborg; 4. Smedvatten, Goteborg; 5. Ski tjarn, Varmland; 6. Blomman, Goteborg; 7. Sodra Blotevatten, Bohuslan; 8. Bredvatten, Goteborg; 9. Stensjon, Varmland; 10. Grytsjon, Orebro; 11. Ekelidvattnet, Bohuslan; 12. Nedre Sarnamannasjon, Jamtland; 13. Tarmalangen; 14. Kolabodasjon, Smaland. For mean retention times shorter than 0.5 years the resulting duration is unstable and sensitive to sudden pH depressions in the tributaries.

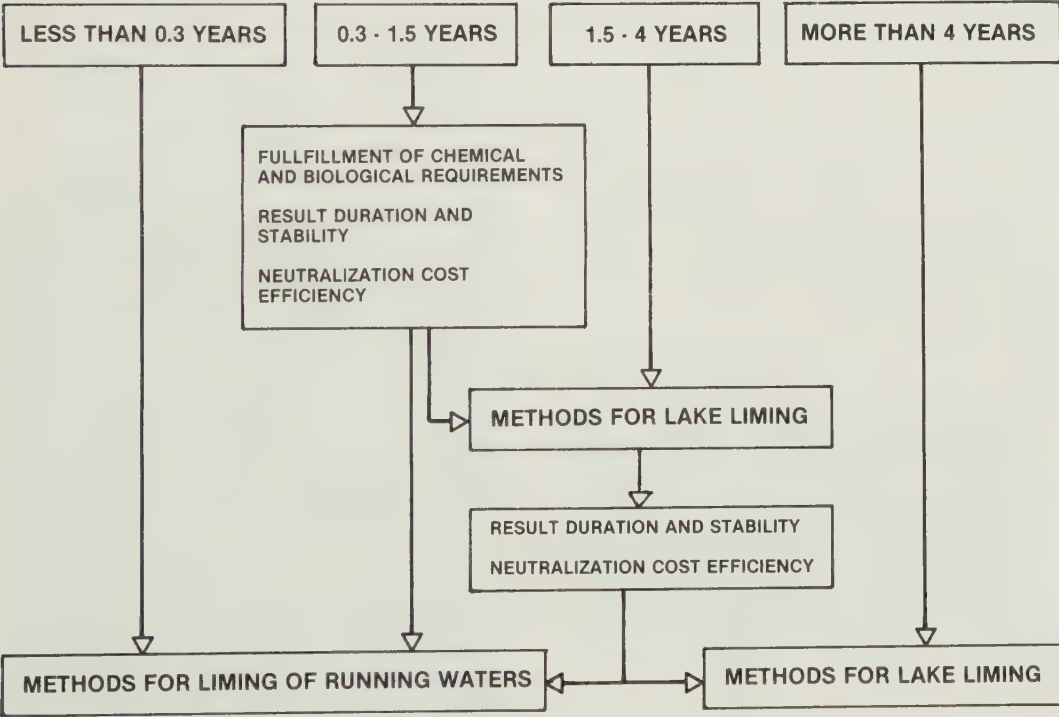


Figure 12.—Flow sheet for deciding between methods for running waters and methods for lake liming.

calcite utilization for coarser powders falls off drastically.

Other methods. There are many other, and in terms of regulation, simpler solutions available in Sweden, such as the Hallefors apparatus or the Borlange apparatus which are smaller and simpler versions of dry-powder, dry application techniques. They usually give a rather low calcite utilization efficiency due to the dry application.

Limestone barriers have been tried on several occasions in Sweden. They very soon clog and fail to work.

Long beds of several kilometers of limestone gravel do not work particularly well either in rivers.

Brook liming with calcite powder usually works for only a limited period and not during spring flood conditions. Projects as Vannear, Anrasan or Hogvadsan in Sweden show this very clearly.

THE PERFORMANCE OF THE DOSING EQUIPMENT

All the mentioned equipment can achieve a correct neutralization of running water as long as it is well designed and adjusted. Most of the regulated equipment works on the flow rate as it is our experience that pH electrodes are very unreliable without tedious maintenance during the winter season in rivers or natural waters.

The calcite utilization differs for the different equipment, and will affect the neutralization cost efficiency.

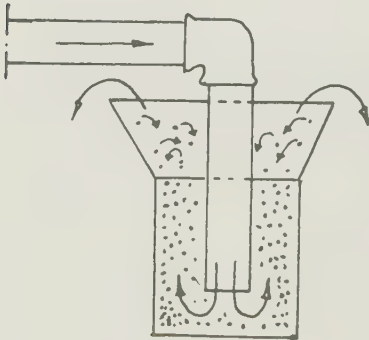


Figure 13.—Schematic view of the diversion well.



Figure 14.—Photograph of the diversion well at Piggaboda.

The calcite utilization efficiency is summarized in Figure 19 together with the calcite utilization for other methods.

LAKE LIMING DEVELOPMENT OF NEW TECHNOLOGY

Conventional lake liming is carried out by boat, and preferably the calcite powder should be well mixed with water prior to spreading. This usually ensures precision and good results. The capacity is approximately 30 to 40 tons of calcite per day.

To improve daily capacity the "Calcade" method was developed. Conventionally a boat must return to base to reload every time its 7 ton supply is exhausted. Instead of using a tank on board, in the Calcade method the boat is outfitted with a long rubber hose and the calcite powder continuously pumped as a slurry to the boat. This raised possible delivery to 150-200 tons per day. When the slurry is pumped at

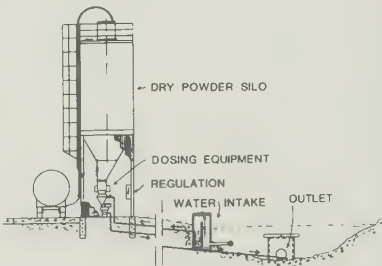


Figure 15.—Schematic view of the dry powder doser at Ryaberg, Fyllean.



Figure 16.—View of the site with the dry powder doser at Ryaberg.

high pressure, the hose can be several km long and all heavy equipment stay ashore by the roadside. The flexibility of the long hose means that the equipment does not even have to be placed on the shore. A distance from the shore of 3 kilometers (or 2 miles) has been tested successfully so far.

A picture of the equipment in use can be seen in Figure 20 where the boat is 1.8 kilometers from the land station. In this project, 9,000 tons of calcite were spread in Stora Lee, a large lake in Varmland, Sweden.

DISCUSSION

Despite the fact that the ultimate goal of a liming project is to preserve or restore ecological or biological communities, the problems encountered in carrying out the project are often of a strictly technical nature.

In complex hydrology or chemical reaction engineering, problems are encountered in almost any liming project. When dealing with dosage apparatus,

regulating problems often appear. Such problems are often more efficiently dealt with by engineers than biologists. It is important that the person planning a liming project has some understanding of the chemical reaction engineering principles and the hydrological principles involved in the dissolution of calcite in natural water systems.

THE FINAL SOLUTION TO THE ACIDIFICATION PROBLEM

What is discussed in this paper does not represent a final solution to the acidification problem. It only gives a perspective of how some of the damage of the en-

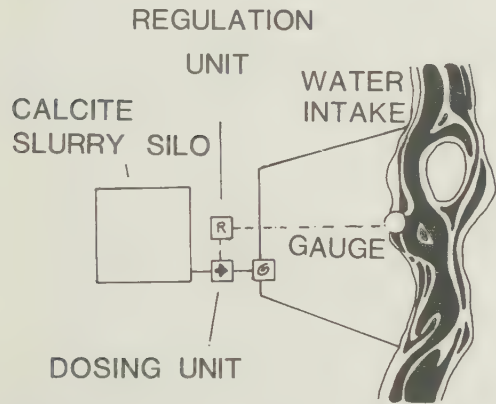


Figure 17.—Schematic view of the Marback slurry doser equipment.

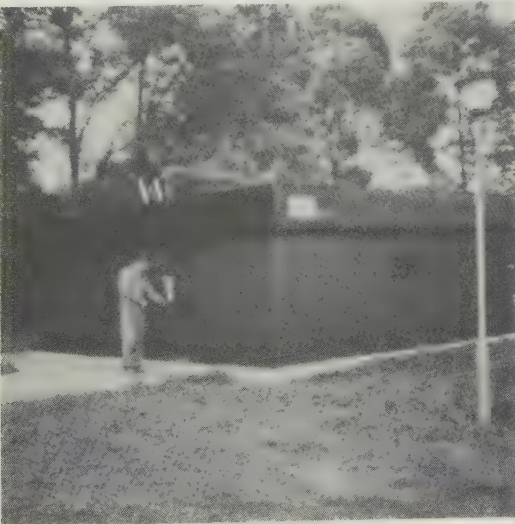


Figure 18.—Photograph of the Marback plant.

TOTAL CALCITE UTILIZATION

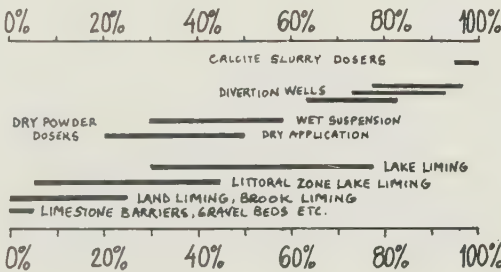


Figure 19.—The calcite utilization efficiency for several liming methods. The reason for the considerable length of the bars is due to the influence of initial pH. The diagram is valid in the pH region from 4.9 to pH 6.5.



Figure 20.—The calcide method, where the boat is supplied from a shore with the calcite powder mixed with water through a long hose. The system has successfully been tested for distances up to 3 kilometers.

vironment can be temporarily and partially repaired. Very severe problems face us in the near future as the acidification of the soil and the ground water proceeds, threatening our water resources and forests. The final solution to the problem must be to reduce the emissions of acidifying agents.



Figure 21.—Conventional lake liming: The Korsnjo-Boksjo lake system was limed with 9,000 tons of calcite powder classified as 0–0.2 mm. The calcite was spread from a boat with a capacity of 14 tons. Then the powder was applied dry. Later it has been discovered that the wet technique will better use the calcite. The "dust bowl" is also avoided.



Figure 22.—The calcite powder should be evenly spread over the lake surface. A very concentrated dose may locally increase the density of the water, and plumes of water–calcite slurry will sink through the water column. The good spread is ensured with the Calcade method, here seen 1.8 kilometers out from the supply station.

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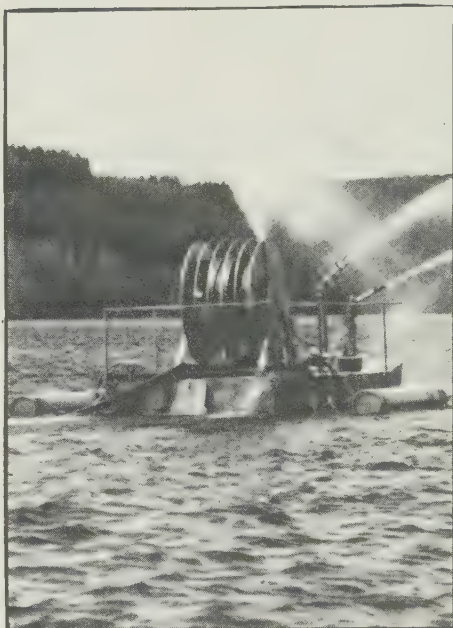
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List of Symbols

A	Constants
A'	Constants
AL	Area of the lake
A _p	Area of a calcite particle
B	Surface load factor for lake liming
C	Hydrogen ion concentration
$\frac{\partial C}{\partial R}$	Concentration gradient around particle

$\frac{\partial C}{(\partial X)}$	Concentration gradient on the boundary layer	$\Delta\phi_i$	Fraction of particles with radium R_i
D	Diffusion coefficient	Q	Flow rate
M	Mass	$\sum_{i=1}^n \frac{\Delta\phi_i}{R_i^3}$	Particle size distribution function
M_0	Initial mass	P	Fraction of the lake area covered in the liming operation
M_i	Mass of fraction i	S	Sinking depth
M_E	Conversion factor	$\frac{\partial S_x}{(\partial t)}$	Sorption rate of calcium to the sediments
$\frac{dM}{dpH}$	Neutralization need	$\psi(t)$	Time dependent inhibition function
$\frac{\partial M}{(\partial t)}$	Dissolution rate	X	Dissolved fraction
$\frac{\partial F}{(\partial t)}$	Flux of calcium from the sediments	Y	Percent carbonate content in calcite
		M^*	Surface load as amount calcite per area treated



A further development of lake liming is represented by the Kalkade method. The calcite powder is pumped from ashore continuously through a hose to the boat. The hose has been successfully operated at distances up to several kilometers and may also provide an alternative for lakes without direct road access. The system has a large peak capacity, 25-40 tons per hour.

